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COMPUTATIONAL MODELING OF ACTIVATION AND DEACTIVATION OF SUPPORTED METAL CATALYSTS.

A Dissertation submitted to the Graduate Faculty

of the University of Virginia in Candidacy for the Degree of

Doctor of Philosophy

by

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Computational Modeling of Activation and Deactivation of Supported Metal Catalysts.

Asanka Wijerathne

(ABSTRACT)

Supported metal catalysts are widely used in heterogeneous catalysis applications such as automobile exhaust gas treatment, petrochemical processes, and biomass conversion. The transition metals that are often used in catalysts are either deposited on support as metal (or oxide) particles or exchanged on or into the support in their cationic form. While both cationic and particle forms could be active for different reactions, their catalytic performances are widely different. Further, cationic species exchanged into zeolites can interconvert between multiple types of monomeric, dimeric, and metallic species under reaction conditions. We used computational methods such as Density Functional Theory (DFT), first principles based thermodynamic calculations, and Monte Carlo (MC) simulations to interrogate the Cu cation speciation in five zeolite frameworks (CHA, MOR, BEA, AFX, and FER). Our thermodynamic analysis shows that frameworks such as MOR possess more exchange site locations that prefer binuclear Cu species, leading to higher populations of Cu dimers than in zeolites such as CHA. Cu exchange free energies calculated for these five zeolites were then extrapolated to 200 other zeolite frameworks using a separate model trained on our calculations. Secondly, we modeled interconversion between metal (oxide) nanoparticles and metal cations observed for Pd exchanged zeolites under hightemperature (593–973 K) oxidizing conditions. Kinetic measurements show that the initial Pd particle size distribution strongly determines the rates of Pd nanoparticle redispersion into Pd^{2+} cations. We explained this strong size dependency quantitatively by combining classical particle growth (Ostwald ripening) theory with an atom trapping reaction. The same mathematical model was then extended to explain Pt metal redispersion (into Pt^{2+}) reported for Pt-CHA, and our kinetic model shows an excellent agreement with experimental data. Moreover, the model reveals the metal particles encapsulated in zeolites have low surface energy, decreasing the driving force for Ostwald ripening and leading to longer catalyst lifetimes. Thirdly, we developed a model for atom trapping processes using a statistical mechanics approach to evaluate the equilibrium state of atom trapping systems. Our results show that the configurational entropy of trapping sites can drive metal particles into the trapping sites on the lattice, even with thermodynamically uphill trapping reaction energies. These findings are consistent with experimental observations and help design catalytic materials with stable performance. Next, we studied the sintering of Pd supported on $\mathrm{Al}_2\mathrm{O}_3$ under oxidative and reductive gas conditions and initial size distributions. Sintering is experimentally quantified using O_2 chemisorption, TEM imaging and C_2H_4 hydrogenation. Then, we used an Ostwald ripening sintering kinetic model to extract kinetic parameters from the experimental sintering data (size vs time). The extracted kinetic parameters revealed that under oxidative conditions, the decreased surface energy of particles (PdO) causes slower sintering, consistent with previous experimental and theoretical observations. Taken together, the mathematical models we developed help estimate the population of cationic and metallic species as a function of material composition and reacting gas environment to help design catalytic materials with improved performance.

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Chapter 1

Introduction

1.1 Significance of Supported Metal Catalysts

Supported metal catalysts such as Pt on silica, Pd on alumina, Pt-Pd-Rh on ceria and transition metals on zeolites are widely used as heterogeneous catalysts for industrial applications such as chemical manufacturing and vehicle aftertreatment systems. The exposed metal area per metal weight decreases with particle size. Therefore, supported metal catalyst's performance is particle size dependent. Undercoordinated surface atoms that are present in higher fractions in small particles generally bind reactant molecules strongly. Moreover, specific atomic ensembles are required for some (structure-sensitive) reactions such as CH_4 oxidation.¹ Therefore, tuning the particle size to achieve maximum activity and selectivity forms the basis for rational catalyst design.^{2,3} Under reaction conditions, these metal active sites undergo structural changes, forming reactive intermediates and catalyzing the reaction. However, unwanted side reactions can also occur, reversibly or irreversibly deactivating the catalyst. Therefore, the optimal catalyst design for prolonged lifetime needs to account for catalyst activation and deactivation mechanisms.

Catalyst deactivation is the decline in catalytic activity and/or selectivity over time. If the deactivation and reactivation are reversible, the deactivated catalysts can be continuously or batch-wise regenerated over cycles, as done in commercial processes such as fluid catalytic cracking and catalytic reforming of naphtha. Therefore, understanding the relationship between the atomic-level structure of supported metal catalysts and catalytic performance is paramount for improving their stability under relevant reaction conditions.

1.2 Catalyst Activation and Deactivation

Catalysts deactivate via thermal, chemical, and mechanical routes.⁴ This dissertation focuses on thermal and chemical activation and deactivation processes in supported metal catalysts.

1.2.1 Chemical Activation

Supported metal catalysts often require a pretreatment (e.g. heat in air, flow H_2 under high T) to generate active sites for a given reaction. Upon activation, ensembles of sites are formed and contribute to the reaction rate (and/or selectivity) to a varying degree. For example, flowing O_2 at high temperatures (T > 700K) activates Cu-exchange zeolites to the partial methane oxidation (PMO) reactions. The nuclearity of the Cu complexes formed upon chemical activation and the specific location of a Cu complex is shown to determine the methane activation barrier.^{5–8} The coexistence of sites with varying degrees of reactivity and their population changes upon exposure to the reaction conditions and have a significant impact on observed reaction rates and, therefore, must be treated properly in thermodynamic and kinetic modeling of these materials.

1.2.2 Deactivation via Chemical Poisoning

Chemical deactivation happens when the active sites strongly react with reactants, products, and (or) impurities. Those chemical species can either block the active sites and (or) change the metal active site structure into an inactive or less reactive structure.^{9–11} Moreover, specific active sites can deactivate faster or slower depending on their interaction with the poison. For instance, multinuclear Cu species in CHA zeolites are more prone to poisoning by SO_2 than mononuclear Cu species.¹²

1.2.3 Thermal Deactivation via Particle Sintering

Supported metal catalysts are often exposed to high temperatures and reactive chemical species. These conditions cause highly dispersed single atoms and atomic clusters to aggregate into larger nanoparticles or, smaller nanoparticles to grow larger over catalyst lifetime. Overall, it reduces the metal particle size, and the amount of metal sites that are accessible for reactants declines over time, decreasing the reaction rates. This particle growth is referred to as sintering, and it follows two pathways:(1) Ostwald ripening and (2) particle migration and coalescence (PMC). OR is driven by gas phase or surface-mediated metal monomer diffusion between relatively immobile supported nanoparticles.^{13–15} In contrast, mobile particles, mostly single metal atoms or smaller clusters coalesce into larger particles in PMC.¹⁶ The relative contribution of OR to PMC in sintering is determined by the metal support interaction strength and the free energy barriers for monomer generation.^{16,17}

1.2.4 Particle Redispersion

Particle redispersion is the reverse process of sintering where nanoparticles disintegrate into small clusters or isolated sites (single metal atoms). If the reaction requires ensembles of more than one metal atom, this redispersion can cause catalyst deactivation. Particle sintering and redispersion are affected by: (1) Temperature; (2) gas environment (e.g. CO causes complete disintegration of Rh on CeO_2); (3) metal-support interactions characterized by the particle adhesion energy; and, (4) the density of 'trapping sites' or defects on the support.

1.3 Aluminosilicates in Heterogeneous Catalysis

Aluminosilicate materials, mainly alumina (Al_2O_3) and zeolites, are widely used in heterogeneous catalysis due to their cheap, scalable synthesis, high thermal and chemical stability, and high porosity (and or specific surface area). Different Al_2O_3 phases, such as γ - Al_2O_3 , $\theta\delta$ - Al_2O_3 have been used in catalysis, whereas the most thermodynamically stable α - Al_2O_3 is less desirable for catalysis applications due to its low specific surface area.¹⁸ Zeolites are crystalline aluminosilicates consists of connected SiO₄ and AlO₄ tetrahedra and charge balancing cations. The metal speciation in zeolites can be controlled by synthesis protocols (Si/Al ratio and Al distribution),¹⁹ gas treatments (hydrothermal aging, calcination),²⁰ and metal loading.^{20–22} Metal species observed in different metal supported zeolites are encapsulated or externally supported metal (or oxide) particles, small atomic clusters (3-10 atoms), cationic framework species (e.g. Ti, Ga) and, extraframework mononuclear and multinuclear cationic species.^{23,24} These species coexist and interconvert with reaction and exposure conditions. In this dissertation, I explore the thermodynamic and kinetic factors affecting metal speciation in aluminosilicate materials, which determine their reactivity, stability, and deactivation.

1.4 Scope of This Dissertation

This dissertation aims to develop a molecular-level understanding of the thermodynamics associated with cation speciation in metal-exchanged zeolites and thermodynamics and kinetics of sintering of supported metal catalysts using computational modeling and tools such as density functional theory (DFT), classical force fields, machine learning potentials, and kinetic Monte Carlo (kMC) simulations.

Chapter 2 presents an extensive study on the Cu cation speciation in different zeolite topologies under varying H_2O pressures and temperatures, which are critical parameters in high-temperature SCR and partial CH_4 oxidation to CH_3OH . Our simulations of the copper dimer and monomer fractions with different Al distributions demonstrate the key role of Al distributions in Cu cation speciation. Moreover, our simulations show that condensation of proximal Cu hydroxyl sites occurs to form water and Cu dimers, consistent with the experimental observations.

Chapter 3 studies a system where extracrystalline Pd nanoparticles convert to ion-exchanged Pd^{2+} in CHA zeolites via redispersion of agglomerates of metal or metal-oxide domains. We found that both the average nanoparticle size and the size distribution, gas conditions such as O_2 and H_2O pressures, and zeolite composition, dictate the thermodynamic extent and rates of conversion. However, the sintering and redispersion kinetic parameters for a given gas condition and zeolite composition were invariant to the particle size distributions. Chapter 4 reports a study on zeolite-encapsulated Pt nanoparticles that redisperse into ion-exchanged Pt^{2+} in CHA zeolites. We used thermodynamic analysis of cationic species and two well-established free energy models (supported and unsupported) for particles to estimate the equilibrium extent of Pd redispersion. While thermodynamic predictions were similar for both free energy models, the regressed kinetic parameters against the experimental redispersion data show better agreement with the supported particle model, indicating that the zeolite pore strongly interacts with the surface atoms of the particle. We found that the zeolite encapsulation stabilizes the Pt particles and sintering-redispersion by lowering the surface energy. These findings help rationalize experimental approaches of zeolite encapsulation for combating metal sintering.

Chapter 5 is a theoretical study on estimating the thermodynamic limit of nanoparticle redispersion. We investigated many hypothetical material compositions to explore the effect of cation exchange free energy and atom trapping site density on the equilibrium fraction of particle redispersion. We found that previously reported assumptions break down for some material compositions while our predictions remain within physical limits.

Chapter 6 reports a combined experimental and theoretical study on the sintering of Pd supported on different amorphous Al_2O_3 supports under oxidative (10 kPa O_2 , 10 kPa H_2O , balance N_2 at T = 1073 K) and reductive (2 kPa H2, 10 kPa H_2O , balance N_2 at T = 1073 K) treatment conditions. The gas environment and Pd particle size distributions significantly impact sintering rates, while the support properties have a negligible impact on Pd sintering. We used an Ostwald ripening model to extract kinetic parameters from the experimental sintering data (size vs time). The extracted kinetic parameters show that under oxidative conditions, the slower sintering rate is caused by the decreased surface energy of particles (PdO), which is consistent with experimental and theoretical observations. These findings help formulate strategies to minimize Pd sintering to design materials for automotive emissions control catalysts with improved metal utilization for extended lifetimes.

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Chapter 2

Competition between Mononuclear and Binuclear Copper Sites across Different Zeolite Topologies.

This chapter has been reproduced in its entirety with permission from Wijerathne, A.; Sawyer, A.; Daya, R.; Paolucci, C. Competition between Mononuclear and Binuclear Copper Sites across Different Zeolite Topologies. *JACS Au.* **2024**, 1, 197-215. Copyright 2024 American Chemical Society. The supplementary materials for this paper are available at https://pubs.acs.org/doi/10.1021/jacsau.3c00632?goto= supporting-info. This chapter investigates the zeolite framework's thermodynamic preference to form mononuclear Cu vs binuclear copper species under different reaction environments. We investigated the Cu speciation in different Al distributions of selected parent zeolites (CHA, MOR, AFX, FER, BEA) using DFT calculations, accelerated minimum energy structure sampling via machine learning potentials, thermodynamic modeling, and Monte Carlo simulations.

In this work, I did DFT calculations, trained the machine learning potentials, and performed Monte Carlo simulations to predict the population of Cu species under a variety of reaction conditions. As the first author of this paper, I also played a lead role in drafting and editing the manuscript, writing the Introduction and results sections, and modifying the manuscript by addressing reviewer comments.

2.1 Introduction

Active site heterogeneity is a key concept in heterogeneous catalysis and a primary challenge is identifying active sites and their distribution.¹⁻⁴ Active site heterogeneity can stem from differences in ligands and atomic environments,^{1,5-7} including variations in the nuclearity of metal active sites.⁸⁻¹¹ Materials containing a distribution of metal active site nuclearities can show drastic differences in reactivity for reactions including ethylene hydrogenation,¹²⁻¹⁴ D₂ exchange in CH₄,¹⁵ and partial methane oxidation (PMO).^{8,16-22} Copper-exchanged zeolites in particular have shown sensitivity to active site nuclearity for a number of reactions including the selective catalytic reduction (SCR) of NO_x^{4,23,24} catalytic or step-wise PMO,^{16,18,20} and NO oxidation.²⁵ Here, we develop condition-dependent computational models for Cu speciation in a wide variety of zeolite topologies and compositions. We use our models to rationalize reported trends and observations in a wide body of experimental literature, and determine specific zeolite topologies that favor the formation of either mononuclear or binuclear Cu complexes.

The nuclearity of ion-exchanged Cu is sensitive to structural and compositional features of the zeolite host. Zeolites are nanoporous aluminosilicates consisting of TO_4 tetrahedral primary building units (T=Si or Al), which connect to form different size rings and cages known as secondary building units (SBUs) that comprise different 3D crystalline zeolite topologies (Figure 2.1). Substitution of Al in the zeolite lattice creates anionic sites ([AlO₂]⁻) that are charge compensated by extra framework cations. The speciation of those cations is dictated by the arrangement of anionic Al configurations^{26–30} and exposure conditions.^{29–32} For example, in the presence of H_2O at low (<473 K) temperatures, these cations form solvated complexes detached from the zeolite framework, such as $[Cu(H_2O)_4]^{2+}$, and are less sensitive to specific Al arrangements and zeolite topologies.^{31,33,34} However, at higher temperatures, Cu ions bond to the zeolite framework and form structures such as $Z_2^{2-}Cu^{2+}$ or Z^-Cu^+ , where Z denotes an anionic charge ($[AlO_2]^-$) in the zeolite framework.^{4,31,35} The parent zeolite's Al distribution is mainly determined by the synthesis conditions,^{28,36,37} although post-synthesis protocols such as hydrothermal aging and dealumination can alter the Al distribution.^{38–40} However, once the parent zeolite is synthesized with charge-compensating cations such as Na⁺, H⁺, or NH₄⁺, literature evidence suggests^{1,3,23,41} that the thermodynamics of Cu cation exchange largely dictates the formation of different Cu sites because framework Al is relatively immobile under typical ion exchange conditions.^{41–43}

The nuclearity and ligand environment of Cu sites depend on exposure conditions, Al distribution, and zeolite topology.^{1,4,23,32,44–46} Figure 2.1a shows CHA and MOR, two zeolites that are topologically different (other zeolite topologies are discussed below). We hypothesized that these topological differences may result in variation of Cu speciation, even at similar compositions (Si:Al and Cu:Al). For example, Z_2Cu monomers (Figure 2.1b) preferentially occupy 2Al configurations in six-membered rings (6MR) in CHA^{27,31,47,48} and other zeolites,^{36,49} while 8MRs in CHA, MOR, and other zeolites such as MFI and MAZ, appear to demonstrate a preference for multinuclear Cu species (Figure 2.1c).^{18,32} Isolated Z_2Cu sites have been shown to be inactive for partial methane oxidation (PMO) reactions,^{18,50,51} whereas multinuclear Cu species,^{18,52–55} or proximal mononuclear Cu species,⁵⁶ are suggested as active sites. Although the exact nature of Cu active sites for PMO is debated, various forms



Figure 2.1: Different ring structures and extra-framework Cu species present in zeolites (a) CHA framework (top) and MOR framework (bottom) , (b) Cu-monomer species , (c) Cu-dimer species.

of multinuclear Cu sites, and Cu dimers most commonly, have been implicated as active sites.^{8,18,32,52,53,57} The abundance of multinuclear Cu species in zeolites such as MOR could in part explain their higher methanol yields (per Cu) compared to other zeolites such as CHA,^{18,52} where redox-resistant isolated Z_2 Cu species may inhibit PMO reactivity. Similarly, for high temperature (>523 K) SCR and oxidation of NO or NH₃,^{11,25,58,59} framework-coordinated Cu dimers in CHA have been implicated as active sites, and their number and speciation may impact high temperature performance when comparing zeolites with different Al distributions and topologies. While these observations support zeolite composition and topology as important factors in Cu speciation, many unknowns remain. Why does MOR appear to have a higher population of multinuclear Cu species than CHA at most compositions? More broadly, why (at equivalent exposure conditions) do certain Al distributions and zeolite topologies show a preference for forming Cu monomers or dimers, and can this preference be predicted?

Here, we use a combination of machine learning-based interatomic potentials, DFT calculations, and Monte Carlo simulations, to estimate the relative populations of different Cu species across a wide variety of zeolite topologies. We show that the nuclearity of Cu species depends sensitively on temperature and the availability of specific 2Al configurations, and the multiplicity of these configurations is zeolite topology-dependent. Our results rationalize experimentally observed differences in PMO performance between different zeolites, and experimentally quantified variations in Cu dimer populations as a function of temperature and topology. Finally, we show that a machine learning-based classification model, using geometry and void space descriptors, is capable of discriminating the propensity to form mononuclear or binuclear Cu sites at specific 2Al configurations in zeolite topologies across the international zeolite database (IZDB).

2.2 Results and Discussion

2.2.1 Al Configuration-Dependent Free Energies of Cu Motifs

Extra framework Cu cations charge-compensated by zeolite framework Al (Z) can form either mononuclear or multinuclear complexes. The type of complex formed is dictated by the sample history and external conditions (temperature and pressures), the macroscopic composition of the zeolite (Si:Al and Cu:Al), and at a given composition, the distribution of Al arrangements. Ensembles of multiple Al result in a distribution of environments for cation siting. To make the resulting configurational space tractable, we limit our analysis to 1Al and 2Al configurations, oxidizing hydrothermal conditions (O- and H- containing Cu motifs) relevant to chemistries such as PMO and high-temperature SCR, and monomer and dimer Cu nuclearities. To determine the relative likelihood for different Cu species to form in a variety of zeolite topologies (vide infra), we computed Cu exchange free energies (all energies were computed using DFT, see Methods and Section S5 for free energy approximations) at each symmetry distinct 1Al, and 2Al configuration within an Al-Al separation distance of 10 Å. At distances longer than 10 Å, both Al are treated as functionally isolated 1Al sites, and are assumed to exchange only ZCuOH (see Methods). For each 2Al configuration the computed Cu motifs (Figure 2.1b,c) included monomers: Z_2Cu and 2 ZCuOH, and dimers: Z_2Cu_2O , $Z_2Cu_2O_2$ (trans, cis, and $\eta^2: \eta^2$ isomers), Z_2Cu_2OH and $Z_2Cu_2(OH)_2$. These species were selected because they are the most thermodynamically stable Cu²⁺ motifs reported in previous experimental and computational studies over a wide range of oxidizing conditions,^{17,31,32,35,48,60–65} although under some oxidizing conditions, a minority fraction of these species may "autoreduce" to ZCu (*vide infra*). For a given Cu motif and Al configuration, the free energy to exchange Cu for the Brønsted acid sites in the proton form zeolite can be computed for a set of gas conditions (T, P_{H_2O} , P_{O_2}) and relative to a Cu reference state. We chose CuO(s) as a convenient reference state, which results in the following general equation for cation exchange:

$$\mathbf{Z}_{2}\mathbf{H}_{2}(\mathbf{s}) + x \operatorname{CuO}(\mathbf{s}) + \frac{(2 y - 2 x - z + 2)}{4} \mathbf{O}_{2}(\mathbf{g}) + \frac{(z - 2)}{2} \mathbf{H}_{2}\mathbf{O}(\mathbf{g}) \xrightarrow{\Delta G_{\text{species}}} \mathbf{Z}_{2} \mathbf{Cu}_{x} \mathbf{O}_{y} \mathbf{H}_{z}(\mathbf{s})$$

$$(2.1)$$

For example, this equation reduces to the following for three of the possible Cu motifs:

$$Z_2H_2 + CuO \xrightarrow{\Delta G_{Z_2Cu}} Z_2Cu + H_2O$$
 (2.2)

$$Z_2H_2 + 2 \operatorname{CuO} \xrightarrow{\Delta G_{Z_2Cu_2O}} Z_2Cu_2O + H_2O$$
(2.3)

$$Z_2H_2 + 2 \operatorname{CuO} \xrightarrow{\Delta G_{2 Z C u O H}} 2 Z C u O H$$
 (2.4)

DFT energies were computed for all Z_2H_2 structures with different 2Al configurations, and details of the free energy calculations, structure generation, and sequential optimizations for all Cu-containing structures are reported in Methods, Sections S2 and S4. The result of these calculations is an exchange free energy for each of the six Cu motifs at each 2Al configuration (e.g. the 21 2Al configurations in CHA, Figure 2.2a, result in 150 computed free energies).

To evaluate the probability of forming a certain Cu species (s) relative to others at a given aluminum configuration (i), we used the relative exchange free energies $(\Delta G_{i,s})$ for each species and assumed they follow a Boltzmann distribution and are kinetically accessible. Therefore, the probability $(p_{i,s})$ for species s to form at 2Al site i is:

$$p_{i,s} = \frac{\exp\left(\frac{-\Delta G_{i,s}}{RT}\right)}{\sum_{s}^{\text{All Cu species}} \exp\left(\frac{-\Delta G_{i,s}}{RT}\right)} .$$
(2.5)

This approach does not assume any Al distribution and gives Cu speciation probabilities for all 2Al configurations in each zeolite. To begin, we chose CHA and MOR (other zeolite topologies are discussed later) due to their topological differences (Figure 2.1a) and because previous studies have shown that Cu-dimers are the majority Cu motif in MOR at a wide range of compositions,^{8,66–68} whereas prior experimental and computational results show Cu preferentially occupies the 6MR in CHA forming Z_2 Cu monomers.^{27,31,47,48,69,70}

Figure 2.2a and b report the Cu speciation predictions for each distinct 2Al configuration in CHA and MOR, respectively, at 973 K, 10^{-6} kPa H₂O and 20 kPa O₂. This condition is representative of a high-temperature oxidative treatment in dry air, and yields analogous results to 773 K at 10^{-8} kPa H₂O and 20 kPa O₂ (other conditions at lower temperatures and variable H₂O kPa are explored below and in Section S6). For ease of visualization the summed probabilities for both monomers are compared to the summed probabilities of the four dimers, and the most exergonic monomer and dimer exchange energy for each 2Al configuration is reported in Figure 2.2c. Each square in the grid represents a 2Al configuration and all 2Al configurations are treated as equally likely here. The squares are ordered in ascending order of Cu exchange



Figure 2.2: Probability of dimer formation computed by equation 2.5 at 10^{-6} kPa H₂O, 20 kPa O₂ at 973 K, for (a) the 21 symmetrically unique 2Al configurations in CHA and (b) the 100 symmetrically unique 2Al configurations in MOR. Each square in the upper two panels represents symmetrically unique 2Al configurations in ascending exchange free energy order as numbered in the upper left panel. Schematics of respective 2Al configurations for CHA are shown in (a) lower panel. (c)The lowest Cu²⁺ exchange free energies of monomers and dimers computed using equation 2.1 for each 2Al configuration within an Al-Al distance of 10 Å and the marks that form linear columns with roughly constant monomer exchange free energies are 2Al configurations that have 2 ZCuOH Figure S4.3 as the most stable monomer.

free energies (using the most exergonic exchange energy amongst all Cu species) from left to right, and top to bottom, as numbered in Figure 2.2a upper panel, placing the most thermodynamically preferred exchange reaction amongst all 2Al configurations in the top-left corner and the least favorable in the bottom-right corner. The equilibrium populations of Cu monomers and dimers will depend on both the relative exchange energies and the abundance of specific 2Al exchange configurations, which is explored in the next section. For CHA the 3NN-6MR configuration has the lowest Cu exchange free energy (Figure 2.2a, lower panel) followed by the 2NN-6MR configuration, and both configurations exchange Cu as Z_2 Cu monomers consistent with prior studies.^{27,31,70,71} Similarly, in MOR, the lowest Cu exchange free energy occurs at a 2Al site in a 3NN-6MR configuration located in the side pockets of MOR (Figure 2.1a) and exchanges Cu as a Z_2 Cu monomer (Figure 2.2b). In both zeolites, the lowest free energy Cu dimers are predominately located at 8MR 2Al sites, and dimers form only up to 2Al separation distances of 8.2 Å and 9.4 Å, in CHA and MOR, respectively (Figure S5.1). These results show that both CHA and MOR have several 2Al exchange sites that preferentially exchange either monomers or dimers; rationalizing the observed differences in Cu speciation between the two zeolites requires knowledge of the 2Al configuration multiplicities and the Al distribution.

Figure 2.2c shows the most exergonic exchange energy for a monomer and dimer at each 2Al configuration in CHA and MOR. The competition between dimer and monomer formation at each 2Al configuration (i) is dictated by these relative exchange energies, as indicated by the blue and red shaded regimes separated by the purple line $(\Delta G_{i,\text{monomer}} = \Delta G_{i,\text{dimer}})$ in Figure 2.2c. For example, if the monomer exchange free energy is less than the dimer exchange free energy ($\Delta G_{i,\text{monomer}} < \Delta G_{i,\text{dimer}}$), that 2Al configuration thermodynamically favors Cu monomer exchange, and vice versa.
The upper right quadrant shows configurations that exchange Cu endergonically at these conditions, which for CHA consists of 7 2Al configurations (7-2ZCuOH), and for MOR 11 configurations (11-2ZCuOH). Thermodynamically, Cu speciation will be biased toward more exergonic 2Al exchange configurations and corresponding species for a given zeolite, provided that each 2Al configuration is available in the zeolite.

2.2.2 Cu Speciation as a Function of Zeolite Composition

To assess equilibrium macroscopic Cu speciation as a function of Si:Al and Cu:Al in CHA and MOR zeolites at 973 K, 10^{-6} kPa H₂O and 20 kPa O₂, we used Monte Carlo (MC) simulations^{31,72–75} as detailed in Methods. In brief, using an ensemble of large zeolite supercells, we titrate 2Al sites with Cu motifs according to the computed Cu exchange free energy probabilities (eq. 2.19, more exergonic exchange free energies correspond to higher probabilities), and record the identities of the Cu species and the 2Al configurations they populate. The aluminum distribution of a zeolite depends on the synthesis protocol^{28,76,77} and post-synthetic modifications.^{37–40,78–80} We initially assumed a pseudo-random aluminum distribution (referred to as random Al) in our MC simulations, other Al distributions are explored further below. We excluded the 1NN 2Al configurations when populating Al because such 2Al pairs are unlikely to form in synthetic zeolites according to Löwenstein's rule.⁸¹

Figure 2.3 reports the computed fraction of Cu corresponding to each species (divided by total Cu) for varying Cu:Al and Si:Al compositions. In CHA (Figure 2.3a), Z_2Cu monomers are the majority species at low Cu loading and Al rich compositions, consistent with ca. zero Cu dimer formation probabilities at these sites for CHA (Figure 2.2a). However, the fraction of Z_2Cu monomers decreases as Cu:Al and Si:Al



Figure 2.3: Predicted Cu speciation for a random Al distribution at conditions of 10^{-6} kPa H₂O, 20 % O₂ at 973 K (a) in CHA zeolite and (b) in MOR zeolite as a function of material composition (Si:Al and Cu:Al). The Cu dimer heatmaps report the summation of all types of dimers shown in Figure 2.1c. The population of all Cu species in Cu-CHA and Cu-MOR with fixed Si:Al=12 as a function of Cu:Al is shown in the bottom panels.

ratios increase in CHA, due to saturation of the available 6MR 2Al sites. The Cu:Al and Si:Al values that 6MR 2Al sites saturate with Z_2Cu at are identical to previous studies.^{31,75} With increasing Cu loading, the fraction of Cu dimers increases, with a maximum population of Cu dimers (0.49) reached at Si:Al=21 and Cu:Al=0.26. This saturation phenomena is similar to Cu-exchange of zeolite-Y,⁸² where Cu is first exchanged as Cu^{2+} monomers at proximal 2Al sites and at increasing Cu loading forms primarily $[Cu-O-Cu]^{2+}$ dimers separated by longer Al-Al distances. Conversely, in MOR the majority Cu species are dimers (Figure 2.3b) and the total fraction of Cu dimers is close to constant over a wide range of Cu loadings (Cu:Al<0.6) and Si:Al ratios (Si:Al<40). For a given Si:Al, the saturation of Z_2Cu in CHA (Figure 2.3a) indicates that the $\rm Z_2Cu$ population is limited by the availability of 6MR 2Al exchange sites (2Al configurations 1 and 2 in Figure 2.2a) in a random Al distribution whereas, the constant dimer fraction in MOR indicates the abundance of 2Al sites in a random Al distribution that preferentially exchange Cu as dimers. Nevertheless, at the highest Si:Al and Cu:Al (upper right corner of the heatmaps), ZCuOH monomers are the majority species in both zeolites, due to the low number of Al per unit cell, statistically limiting (for a random Al distribution) the formation of 2Al sites within 10 Å , which are required to form either Z_2Cu monomers or Cu dimers as detailed in Section S5.3.

The fraction of Cu dimers depends on the zeolite topology; for all compositions the fraction of Cu dimers is higher in MOR than in CHA (Figure 2.3a,b). This difference stems from MOR facilitating dimer formation even at low Cu:Al, whereas in CHA, Cu dimers populate only after a threshold Cu loading (that increases with decreasing Si:Al) is achieved due to saturation of 6MR 2Al configurations. In MOR, despite the lowest exchange free energy 2Al configuration forming Z_2Cu monomers, a Cu:Al threshold for dimer formation does not exist because the lowest energy Cuexchange 2Al configuration (upper-left square in Figure 2.2b) has a lower statistical probability of occurrence than other 2Al configurations that form dimers with slightly higher exchange energy (+5-20 kJ mol⁻¹, see Figure S7.1b) due to differences in the multiplicities of the four symmetry distinct T-sites in MOR.

At high temperature and dry conditions (973 K, 10⁻⁶ kPa H₂O and 20 kPa O₂), Z₂Cu₂O accounts for >90% of all dimers across a wide range of compositions in both CHA and MOR zeolites (Figure 2.3-bottom). Consequently, independent MC simulations at these conditions with only Z₂Cu, ZCuOH and Z₂Cu₂O species show only a small decrease (\approx 5%) in the total dimer population (Section S6.6). These results suggest that Z₂Cu₂O is a reasonable computational probe for estimating the equilibrium total dimer fraction at high temperature dry conditions. Moreover, previous experimental studies have shown spectroscopic evidence for Z₂Cu₂O as the majority Cu dimer site in Cu-MOR,^{61,66,68,83} Cu-MFI^{53,84,85} and zeolite-Y⁸⁶ following exposure to high temperature dry air treatments. Therefore, for the next set of widely used zeolites we studied, BEA, AFX, and FER, we used computed free energies for only Z₂Cu, ZCuOH, and Z₂Cu₂O species.

Figure S6.2 shows the dimer formation probabilities for BEA, FER, and AFX. The AFX zeolite has a probability map similar to CHA, where the lowest energy Cu exchange 2Al sites are Z_2 Cu monomers, followed by dimers and ZCuOH. Consequently, the MC-generated composition diagrams for AFX, shown in Figure S6.3b, are very similar to that of CHA, which is unsurprising because CHA and AFX have similar ring sizes, the same SBUs, and share the same double six-membered ring composite building unit, although the connectivity and the cage sizes are different.⁸⁷ Zeolite BEA, a large pore zeolite with 12-6-5-4 rings, has a much lower number of

2Al sites that preferentially form dimers (Figure S6.2c and S6.3a) compared to CHA, MOR, and AFX zeolites at similar conditions. FER and MOR have different ring topologies, yet MC simulations reveal the Cu speciation in both zeolites show no threshold Cu:Al required to form dimers, despite Z_2Cu monomers being the most exergonic Cu species in both zeolite topologies. Lack of a Cu:Al threshold for dimer formation indicates that, for a random Al distribution, 2Al sites that preferentially exchange Cu^{2+} dimers are abundant in both zeolites (Section S7). However, more ZCuOH form in FER (Figure S6.3c) than in MOR at similar compositions and conditions. Although these MC simulations with random Al distributions serve as a useful benchmark, both synthetic Al distributions (discussed below) and kinetic limitations for reaching equilibrium Cu dimer populations will play a role in determining Cu speciation.

2.2.3 Temperature Effects on Cu Speciation

Figure 2.4 reports the temperature-dependent Cu speciation (from MC simulations at different temperatures) for CHA and MOR at fixed compositions (Si:Al =12 and Cu:Al =0.4, 2.1 wt% Cu) representative of commonly reported synthetic zeolites.^{18,80,88,89} The Z₂Cu fraction is roughly constant across different temperatures in both zeolites. At temperatures below 700 K, the majority of dimers are Z₂Cu₂(OH)₂. As temperature rises from 600 K to 1000 K, the Z₂Cu₂(OH)₂ and ZCuOH populations decrease, and the Z₂Cu₂O population increases. The increasing population of Z₂Cu₂O is entropically driven through liberation of water by the reactions:



Figure 2.4: Temperature dependence of Cu speciation at 10^{-6} kPa H₂O, 20 % O₂ for a random Al distribution in (a) CHA and (b) MOR. Compositions for simulations were fixed at Si:Al=12 and Cu:Al=0.4 for both zeolites.

and

$$2 \operatorname{ZCuOH} \Longrightarrow \operatorname{Z}_2 \operatorname{Cu}_2 \operatorname{O} + \operatorname{H}_2 \operatorname{O}$$

$$(2.7)$$

Consistent with this role of H_2O , Figure S6.6 shows that the temperature where $Z_2Cu_2(OH)_2$ and 2ZCuOH transition to Z_2Cu_2O depends sensitively on H_2O pressure. Lower H_2O pressures $(10^{-7} - 10^{-8} \text{ kPa } H_2O)$ promote formation of Z_2Cu_2O at lower temperatures. Only ZCuOH pairs charge-compensating 2Al within a maximum separation of 8.2 Å (CHA) and 9.4 Å (MOR) of each other (Section S5.3) convert to Z_2Cu_2O with increasing temperature; further than these distances, 2ZCuOH remain lower in free energy than possible dimers.

Spectroscopic and kinetic experiments have suggested that 2 ZCuOH monomers may convert to Cu dimers^{33,44,48,58,63,68,90–92} under a variety of reaction conditions. Pappas *et al.*⁵⁰ observed a decrease in ν CuOH (ca. 3650 cm⁻¹) using in-situ FT-IR, and a concomitant increase in Raman features assigned to Z₂Cu₂O from 523-673 K

in their CHA materials. Similar observations and proposals of monomeric sites converting to dimers have been invoked for MOR using XANES,⁶¹ CO-TPR,⁶⁸ electron paramagnetic resonance, operando-UV/Vis, in-situ photoluminescence, and FT-IR.⁵⁶ Moreover, the proximity of ZCuOH sites, altered by varying Si:Al and Cu:Al for a given zeolite, has been identified as an important factor for achieving higher methanol yields (per mol Cu).^{50,93} This proximity requirement is consistent with our finding that only 2Al configurations within Al-Al separations of ${<}8.2$ Å (CHA) and ${<}9.4$ A (MOR) convert to dimers (Figure S5.1) at high temperatures. Therefore, our temperature-dependent MC simulations corroborate such monomer-to-dimer conversions and predict the majority of ZCuOH monomers will convert to dimers in the 600-900 K temperature range in both CHA and MOR. Kvande et al.⁶⁸ inferred (using in situ XAS during CO-TPR) that proximal ZCuOH may be depleted by ca. 673 K in MOR. Similarly, Pappas et al.⁵⁰ observed a gradual decrease in ν CuOH from 523-673 K in CHA, and the ZCuOH population continued to slowly decrease when temperature was held at 673 K for 150 minutes. Although our MC simulations for both MOR and CHA predict a decrease in proximal ZCuOH pairs and $\rm Z_2Cu_2(OH)_2$ populations in the same temperature range the above authors observe, our thermodynamic models suggest that conversion of these species to Z_2Cu_2O will continue past 673 K, and kinetic limitations for proximal ZCuOH to dimerize may play an important role.

Our simulation results at 10^{-6} kPa H₂O for CHA and MOR both predict Z₂Cu₂(OH)₂ persisting as the majority dimer species until ≈ 750 K, which is ≈ 100 K higher than conditions where Z₂Cu₂O has been reported the majority dimer species.^{50,61,68,94} This discrepancy between the simulated and experimental temperatures for the transition between Z₂Cu₂(OH)₂ and Z₂Cu₂O likely reflects differences in the actual H₂O pressure for dry air treatments, which is challenging to quantify experimentally. Simulations spanning $10^{-4} - 10^{-10}$ kPa H₂O (Figure S6.6) show that Z₂Cu₂O becomes the majority species at 773 K when the H₂O pressure is $\leq 10^{-7}$ kPa, and will require even lower temperatures to become the majority Cu species with a continued decrease in H₂O pressure. Thus, the trend of increasing Z₂Cu₂O populations with increasing temperature (and decreasing H₂O pressure) is consistent with many reports, and may rationalize the need for high-temperature oxygen-activation treatments in PMO cycles.

Our MC model for Cu speciation makes two assumptions that may be violated due to kinetic factors or the presence of Cu⁺. The population of peroxides $(Z_2Cu_2O_2)$ is likely underestimated at lower temperatures because our model ignores kinetic limitations, so even if mechanistically peroxides form first and then convert to other species,^{50,94,95} the peroxides could be trapped at lower temperatures before converting to more thermodynamically stable species at higher temperatures. At the highest temperatures, the population of peroxides increases due to the weak entropic driving force from the exchange reaction:

$$Z_2H_2 + 2 \operatorname{CuO}(s) + \frac{1}{2}O_2 \xrightarrow{\Delta G_{Z2Cu2O2}} Z_2Cu_2O_2 + H_2O$$
(2.8)

however, desorption of O_2 from Cu will also be entropically favored at high temperatures, potentially resulting in some amount of Cu⁺:

$$Z_2 Cu_2 O_2 \rightleftharpoons 2 ZCu + O_2, \qquad (2.9)$$

which is not captured in our model due to exclusion of Cu^+ species. Minority fractions of Cu^+ are commonly reported following high-temperature oxidative treatments. The mechanism and kinetics for this "autoreduction" phenemona are debated, but Cu speciation and proximity have been implicated as important factors.^{8,96}

2.2.4 Cu Speciation for Nonrandom Al Distributions

Only certain zeolite types, such as CHA synthesized with specific protocols, evidence a pseudo-random aluminum distribution^{97,98} whereas zeolites such as commercial MOR commonly show non-random Al distributions.^{Dedecek2012, 99–101} The organic structure directing agents (SDA), inorganic cations present in the synthesis media, and synthesis conditions (temperature and time) largely determine the Al distribution.^{28,97,102,103} Although quantifying the populations of specific 2Al configurations remains a challenge, techniques such as Co²⁺ titration,^{39,97} High-field ²⁷Al NMR,^{80,104} and a combination of X-ray absorption and NMR¹⁰⁵ give information on macroscopic Al distributions. For nonrandom (biased) Al distributions, Cu speciation may change significantly due to changes in the populations of 2Al sites that have the most favorable exchange free energies. To test how biasing Al distributions affects Cu speciation, we chose several scenarios where experiments provide additional rules for Al-siting.

We ran MC simulations for CHA at 973 K (673 K simulations are in Section S6.1) that prohibit 2NN-6MR and 3NN-6MR 2Al configurations to populate (the lowest energy Cu exchange sites according to Figure 2.2a), still obey Löwenstein's rule, but otherwise populate Al randomly. The prohibition of these Al pairs has been observed following the synthesis of CHA with TMAda⁺ in the absence of inorganic SDAs such as Na⁺.^{37,97} The probabilities used for MC simulations are the same as Figure 2.2a because the probability of dimer formation for a given 2Al configuration is independent of the macroscopic Al distribution and only depends on exchange



Figure 2.5: Predicted Cu speciation for biased Al distributions at conditions of 10^{-6} kPa H₂O, 20 % O₂ at 973 K for, (a) CHA zeolite and (b) MOR zeolite as a function of material composition (Si:Al and Cu:Al). The Cu dimer heatmaps show the summation of all types of dimers shown in Figure 2.1c. Heatmaps in (b) show large gradients at Si:Al=8 due to the different MOR Al biasing rules used for Si:Al < 8 and Si:Al > 8. Speciation of Cu-CHA and Cu-MOR with fixed Si:Al=12 is shown in the bottom as a function of Cu:Al.

conditions. However, Figure 2.5 shows that the absence of 2NN-6MR and 3NN-6MR configurations in the CHA lattice resulted in significantly higher total dimer fraction (60%-80% of total Cu) than in a random Al distributions (Figure 2.3) and a

negligible amount of Z_2 Cu (<10% of total Cu). The majority of (> 95%) Z_2 Cu that populate are in 4NN-8MR 2Al configurations (configuration 10 in Figure 2.2a) where dimer formation is only marginally exergonic (-4 kJ mol⁻¹) compared to monomer exchange, resulting in a non-zero Z_2 Cu formation probability, and consequently a mixture of dimers and monomers exchange at this 2Al configuration. At Si:Al=12 (Figure 2.3a-bottom), dimers populate in the CHA framework even at low Cu loadings (Cu:Al<0.05), and as Cu loading increases, the total dimer fraction slowly declines at Cu:Al≈0.35 due to the saturation of Al pairs that favor dimer formation and increasing population of ZCuOH. This Cu speciation pattern differs significantly from the a random Al distribution CHA (Figure 2.3a), but is similar to that of a random Al distribution MOR (Figure 2.3b). Referring back to Figure 2.2a,b, once the first two 2Al configurations in CHA are eliminated, Cu are expected to occupy the next lowest energy 2Al configurations, which favor Cu dimers. This results in a macroscopic Cu speciation similar to MOR, but reaches a lower maximum dimer population.

In the second scenario, we ran MC simulations for MOR obeying Löwenstein's rule and prohibiting 2NN 2Al configurations, as observed for 5MR-containing zeolites with Si:Al>8,^{106–110} while constraining Al T-site occupancies to experimentally quantified populations for commercial MOR zeolites (Section S8.1).⁹⁹ Although different experimental methods^{79,99,104} and calculations^{100,111} show varying Al occupancy probabilities (5%-10% deviation), a similar trend in Al occupancy is reported: T3(43%) >T4 (29%)>T1(18%)> T2(10%),^{79,99–101,112} which are significantly different than the theoretical occupancies for a random Al distribution: T3 (16.7%)=T4 (16.7%) <T1 (33.3%)=T2 (33.3%). The abundance of Al in T3 and T4 sites and the absence of 2NN 2Al configurations (for Si:Al>8) in the biased Al distribution gives a higher

dimer population (Figure 2.5b) compared to a random Al distribution (Figure 2.3b). The most thermodynamically favored Cu exchange configuration in MOR is a 2Al T1-T2 pair that exchanges Z_2Cu , and the next most favorable exchange site is T4-T4, which exchanges Cu dimers. This preference is consistent with previous studies that show 2Al sites with T3-T3 and T4-T4 combinations form more stable Cu dimers than T1-T1 or T2-T2 combinations..^{66,101,113} Therefore, increasing the %Al in T4 sites, and decreasing %Al in T1 and T2 sites, contribute to the observed increase of dimers. This effect is further enhanced by the increased multiplicity of other T3- and T4-containing 2Al configurations (Section S7) with slightly higher Cu dimer exchange energies $(5-40 \text{ kJ mol}^{-1})$ than those discussed above because the abundance of such 2Al configurations makes those sites statistically favorable for Cu exchange. The biased Al distribution and higher multiplicity of dimer-preferred 2Al sites may enable MOR to reach close to the theoretical maximum methanol yield of 0.5 $\frac{\text{mol CH}_3\text{OH}}{\text{mol Cu}}$ for Z_2Cu_2O sites, as observed by Pappas *et al.*⁸ (0.47 $\frac{\text{mol CH}_3OH}{\text{mol Cu}}$). Biasing Al distributions could be a powerful synthetic strategy to increase the number of dimeric (or monomeric) Cu species in applications such as PMO, where binuclear sites are desirable. Both MOR and CHA Al biases considered above increase the dimer fraction, and notably, biasing the Al distribution causes CHA to behave similarly to MOR. Even within the same zeolite topology, Al distribution could alter the Cu speciation significantly such that zeolites with the same macroscopic Cu:Al and Si:Al may have dramatically different Cu nuclearities.

For BEA and FER MC simulations, we prohibited Al-O-Si-O-Al for Si:Al >8, consistent with several studies,^{106–108,114} while imposing Löwenstein's rule. However, for Si:Al <8, we only applied Löwenstein's rule as those Si:Al ratios cannot mathematically be achieved without forming Al-O-Si-O-Al sequences. For BEA and FER,



Figure 2.6: Geometric feature distributions for DFT-optimized Z_2Cu_2O (mono- μ -oxo) dimers in CHA, MOR, BEA, and AFX zeolites. (a) Cu-O-Cu angle, (b) Cu-Cu distance and (c) Cu-O_b distance where O_b is the bridging oxygen between two Cu²⁺ ions. Above distributions only include Z_2Cu_2O dimers associated with 2Al configurations that preferentially exchange Cu as dimers, indicated by red squares in Figure 2.2a and b. Distributions including all dimers computed are shown in Section S10.1.

MC simulations for different experimentally observed Al biases are shown in Section S6.4. Al biases forcing 6MRs to contain a lower amount of Al than in a random Al distribution significantly increases the dimer population in BEA (Figure S6.4b,c) and FER (Figure S6.5a,b), similar to CHA. However, the elimination of Al from the T1 site in FER, consistent with the Al bias reported by Dědeček *et al.*¹⁰⁸ yields 100% monomers (Figure S6.5c). These results for BEA and FER reinforce that sample-specific Al distributions can strongly bias the Cu dimer population in a given zeolite.

2.2.5 Topology-Dependent Structural Features of Z_2Cu_2O

Geometric features of Cu dimers, such as Cu-O-Cu angle and Cu-Cu distance, are reported as important parameters for PMO activity^{115–117} and potentially other reactions. Signatures of these geometric features are typically detected using resonance Raman (rR),^{85,118} UV–Vis,^{68,101,116} and EXAFS.^{68,91} To determine how zeolite topology influences geometric features of Z_2Cu_2O dimers, the most populous dimer species at high temperatures, we analyzed DFT-optimized Z_2Cu_2O structures in the five zeolite topologies: CHA, MOR, BEA, AFX, and FER. Experimentally detected distances (EXAFS) and angles are averaged over populated species, therefore, in our computational analysis (Figure 2.6), we exclude dimers that form at 2Al configurations that prefer monomer exchange. For completeness, we include geometric features of all DFT-computed Z_2Cu_2O structures in the Section S10.1.

The violin plots in Figure 2.6 report the distribution of Cu-O-Cu angles, and $Cu-Cu/Cu-O_b$ distances (where O_b is the oxygen bridging two Cu) of Z_2Cu_2O structures. The $Cu-O_b$ distances fall within a narrow range, and the Cu-Cu distances are strongly correlated with Cu–O–Cu angles. We observe a bimodal distribution of Cu-O-Cu angles centered at 120° and 140° for MOR, consistent with previous studies reporting a bimodal distribution for Cu-O-Cu species and angles^{68,101,119} for MOR. These angles do not correlate with spin states, as both parts of the distribution have (Figure S10.2) a mix of singlet and triplet ground states. Vanelderen $et \ al.^{101}$ reported two distinct $[Cu-O-Cu]^{2+}$ sites in Cu-MOR by observing two absorption bands in their O₂-TPD experiments and rR spectra, and estimated Cu-O-Cu angles to be $137^{\circ}\pm1^{\circ}$ and $141^{\circ}\pm1^{\circ}$, based on normal coordinate analysis of the rR vibrations. While we observe both of these Cu-O-Cu angles in our MOR distribution, the smaller Cu-O-Cu angles in our calculations are more skewed towards lower ($\approx 120^{\circ}$) values, consistent with angles reported in their later study on MOR,⁹ which could be a consequence of Al distribution. The Cu-O-Cu angles in CHA show a wider distribution, including 120° and 140° Z_2Cu_2O dimers¹¹⁶ and one outlier at 90° at the 3NN-8MR 2Al configuration. The AFX, BEA, and FER zeolites show narrower Cu-O-Cu angle and Cu-Cu distance distributions compared to CHA and MOR, indicating that the populated dimer sites are more homogeneous in those zeolites.

2.2.6 Correlation between Cu Dimer Fractions and Methanol Yields

Although the methanol produced in cyclic PMO over different zeolites depends on the Al distribution, activation conditions,^{19,55,88,120–124} and Cu-exchange protocol,^{8,125–127} some zeolite topologies,^{18,88,128} and specific compositions for a given topology, have generally been reported to have higher methanol per Cu yields. While we emphasize our goal here is not to determine specific active sites and activities for PMO, we next tested if observed trends in methanol yields correlate with our predicted total dimer populations. We used our MC predicted total Cu dimer fractions at 973 K, where dimer populations have largely saturated, as an upper bound for the total dimers in a zeolite sample with a specific Si:Al and Cu:Al. We used this number as a conservative upper-bound for the total dimer populations because the precise temperature for O₂ treatments varies, and as discussed above, analogous dimer populations are obtained at lower temperatures (673-973 K) with variation of H₂O pressures between $10^{-8} - 10^{-6}$ kPa. Further, higher CH₄ pressures are demonstrated^{19,55,122} to increase the pool of active sites engaged, supporting the use of total dimer fractions as an upper bound.

Figure 2.7 shows the predicted equilibrium fraction of Cu dimers in CHA (random-Al distribution) and MOR (biased-Al distribution) versus experimentally reported $\frac{\text{mol } CH_3OH}{\text{mol } Cu}$ in the literature (additional details in Section S9). We used a random Al distribution for CHA because the reported zeolites either used inorganic SDAs or were commercial samples. Similarly, the reported MOR samples are all commercial, so we used the biased Al distribution discussed above that is representative of many commercial MOR zeolites. For CHA, all reported $\frac{\text{mol } CH_3OH}{\text{mol } Cu}$ fall near to or below the



Figure 2.7: Experimentally reported $\frac{\text{mol CH}_3\text{OH}}{\text{mol Cu}}$ versus the MC-predicted fraction of total Cu dimers at 10⁻⁶ kPa H₂O, 20 % O₂, 973 K for (a) CHA, and (b) MOR. Details for the zeolite compositions and references corresponding to each data point are reported in Section S9.

line demarcating 1 CH₃OH per predicted Cu dimer, showing a correlation between the maximum achievable $\frac{\text{mol CH}_3\text{OH}}{\text{mol Cu}}$ as a function of composition (Si:Al and Cu:Al), and the predicted number of binuclear Cu sites at a given composition. With the exception of one data point with $\frac{\text{mol CH}_3\text{OH}}{\text{mol Cu}} = 0.6$, MOR data also fall near to or below the 1 CH₃OH per predicted Cu dimer threshold, but there is far less variation in the total dimer fraction at different Si:Al and Cu:Al ratios (Figure 2.5b). The majority of experimental data for both CHA and MOR fall well below the line demarcating one CH₃OH per predicted Cu dimer. This result suggests that in most samples only a fraction of the total binuclear Cu sites react with CH₄ to form CH₃OH at the reported O₂ and CH₄ activation conditions, consistent with the observations of many experimental reports.^{8,57,61,68,129}

To compare across MOR, CHA, BEA, AFX, and FER, we used the most common

Al distribution biases described in the literature for each zeolite along with Löwenstein's rule. Specifically, we prohibited Al-O-Si-O-Al configurations for MOR, BEA, and FER, used the Al T-siting bias described above for commercial MOR materials, and random Al distributions for CHA and AFX. Our simulations show that on the extreme ends, MOR has the highest fraction of Cu dimers at all compositions, and BEA has the lowest dimer population, which is consistent with the significantly lower PMO yields reported for BEA compared to CHA and MOR with similar compositions.^{18,19,125,130} The $\frac{\text{mol CH}_3\text{OH}}{\text{mol Cu}}$ values for AFX, FER, and BEA are again near to or below the line demarcating one CH₃OH per model-predicted binuclear Cu site (Figure S9.2). FER methanol yields¹³¹ for a random Al distribution (Figure S9.3b) are far above this threshold, suggesting these FER materials do not contain Al-O-Si-O-Al configurations at Si:Al >8, as reported by previous studies.^{106,108} At a typical composition of Si:Al=12, Cu:Al=0.3 the ordering from most to least Cu dimers is MOR(0.92) >> CHA(0.45) > FER(0.34) > AFX(0.32) > BEA(0.28), consistent with the ordering of the maximum $\frac{\text{mol } CH_3OH}{\text{mol } Cu}$ that is reported for these five zeolites at similar compositions^{18,88,130} (Si:Al 8-15, Cu:Al 0.3-0.5) following cyclic PMO treatments. Caution is warranted for this comparison because of the uncertainty in Al distributions of these materials. Taken together, our results reinforce that the equilibrium population of higher nuclearity Cu species is a factor in determining the maximum achievable CH₃OH yields, however, under the vast majority of cyclic conditions and sample compositions not all of these higher nuclearity Cu sites may be kinetically accessible, reactive, or selective.

2.2.7 Classification of Zeolite Topologies

Differences in zeolite topologies create variations in Al-Al distances, ring sizes, T-site connectivities, and pore volumes, which may determine whether a specific 2Al exchange site populates with mononuclear or binuclear Cu sites. Our MC simulations show that zeolites with 8MRs have more 2Al pairs that exchange dimers (MOR, CHA, and AFX) compared to a zeolite with larger pores (BEA). We aimed to identify such patterns in Cu speciation in a high-throughput fashion using a machine learning model. Similar models have been reported for predictions of mechanical and chemical properties of zeolites and metal-organic frameworks,^{132–134} 2D zeolite constructions,¹³⁵ zeolite-OSDA interactions governing synthesis,^{103,136} and C-H activation barriers at $[Cu-O-Cu]^{2+}$ sites hosted in different zeolites.¹¹⁷ The international zeolite database (IZDB) contains 254 zeolites⁸⁷ (composed of tetrahedral sites) that have been experimentally synthesized, and our goal is to screen these structures and identify zeolites with a strong preference for Cu monomers or dimers. To achieve this aim, we used our prior DFT results to build a predictive model for dimer formation probabilities and applied it to zeolites in the IZDB.

To correlate structural features of a given 2Al site with the preference for that site to exchange Cu as a dimer or monomer, we trained an XGBoost decision tree binary classification model (detailed in Methods) using our DFT-computed dimer formation probabilities for five zeolites (CHA, MOR, AFX, BEA, FER) as the targets of the classification model. Initially, as input descriptors, we used the Al-Al distance (Å) and the nearest neighbor connectivity (one plus the number of T atoms between Al-Al along the shortest path) corresponding to each 2Al configuration (within 10 Å) for all five zeolites, resulting in 322 total training data points (CHA-25 data points, MOR-100, BEA-154, AFX-43, and we held out FER-84 as a validation set). The DFT-computed dimer formation probabilities are rounded to 0 (monomer) or 1 (dimer) to generate the target for this binary model. With these simple descriptors, the model had 80% accuracy (10-fold cross-validation). We hypothesized that an important feature not captured by these descriptors is the volume of void space spanning 2Al. Corroborating our hypothesis, the accuracy of the model improved to 95% after adding void space descriptors, which we derived from random sphere packing in zeolite void space as described in Methods section.



Figure 2.8: (a) Cu exchange free energy as a function of average projected void space and Al-Al distance for each 2Al configuration in the training and validation dataset excluding Löwenstein's rule violations and Al-Al distances > 10 Å. Larger circles represent more exergonic exchange free energies, and the colors show the identity of Cu species populated at the corresponding 2Al site. (b) Classification modelpredicted number of symmetry distinct 2Al sites that preferentially exchange Cu as dimers divided by the total number of symmetry distinct 2Al sites, for 200 zeolites in the IZDB. The five zeolites used for model training and validation are highlighted with green boxes.

Feature importance scores (Figure S11.5) of the XGBoost model show the aggregate score (mean, min, max, std. dev.) of the void space descriptors as the most discriminating feature of the model, followed by NN connectivity and Al-Al distances, which are similarly scored. Figure 2.8a reports the distance (Å) and void space (dimensionless) spanning each of the 318 2Al configurations used to train the model. Red and blue circles indicate preferential exchange of Cu dimers, or monomers, respectively, and the size of each circle reflects the exergonicity of the corresponding exchange reaction. The most stable Cu monomer exchange sites are clustered near Al-Al distances of 5-6 Å with low (0.05) void space, which correspond to exchange at the 6MRs present in all five zeolites, and monomer exchange at 4MRs and 5MRs is unfavorable. The most stable binuclear Cu sites generally fall into two clusters, 5-6 Å with low void space (analogous to monomers), and a broader cluster spanning ca. 7-8 Å and void space > 0.1, roughly double the amount of void space needed for the most stable monomers. These two clusters are representative of the bimodal Cu–O–Cu angle distributions in MOR and BEA (Figure 2.6a), with the lower void space cluster accounting for the shorter Cu–O–Cu angle sites and the one 90° outlier structure in CHA.

Next, we made predictions using this binary classification model for 200 zeolites out of 254 zeolites in the IZDB, excluding 54 zeolites due to the high computational cost of generating graph-isomorphism-derived features for large supercells. For all unique 2Al configurations in each zeolite, the model predicts whether each 2Al configuration (within 10 Å) exchanges Cu as dimers or monomers. For example, there are 100 predictions for MOR (Figure 2.2b). Using these predictions, we defined a metric "Dimer 2Al Site Fraction (f)" that represents how many of those 2Al configurations favor Cu dimer formation:

Dimer 2Al Site Fraction
$$(f) = \frac{\sum w_i p_{i,\text{dimer}}}{\sum w_i}$$
 (2.10)

where w_i is the multiplicity of the *i*th 2Al configuration in the zeolite supercell based on the graph-isomorphism test (Methods and Section S1.1) and $p_{i,\text{dimer}}$ is the binary probability of dimer formation (0 for a monomer and 1 for a dimer) at 2Al configuration i, as predicted by the classification model.

Figure 2.8b shows the model predictions as a histogram, where zeolites have been sorted into f = 0.05 bins. The order of FER, BEA, CHA, AFX, and MOR is generally consistent with their MC simulation results, suggesting this is a reasonable approach for estimating nuclearity preferences for zeolite topologies. Zeolites sharing all SBUs generally appear together, for example, the CHA-AEI-AFT-AFX family of small pore zeolites all appear in the f = 0.35 - 0.45 regime. The majority of zeolites show $f \ll 0.5$, indicating that most known zeolites have higher populations of 2Al configurations that favor monomer exchange, likely a consequence of the commonality of 6MR SBUs across zeolites. At the extreme end, the zeolites OSI, BEC, ASV, and IWR, have zero predicted 2Al configurations that favor dimer formation, indicating that they should only form mononuclear Cu sites, regardless of their Al distribution. These zeolites all have 6MRs, and do not have 8MRs.

In contrast, zeolites favoring binuclear sites are rare, and none of the zeolites has f = 1, indicating that there will always be a possibility of Cu monomer formation. The model identified 2Al configurations in zeolite topologies with 8MRs and no 6MRs as the zeolites with the highest fraction of 2Al configurations that favor dimers, although we note that some of these topologies have not yet been synthesized as aluminosilicates, such as SBN. In zeolites that are not heavily biased towards monomers or dimers, the relative Cu exchange free energy rankings and Al distribution will play an important role in determining Cu speciation, and the descriptors used in this model are incapable of predicting accurate Cu exchange free energies. However, our results discern the important structural features of each zeolite's 2Al environments that lead to equilibrium Cu nuclearity biases, and identify zeolite topologies on the extreme ends as candidates for further computational and experimental exploration.

2.3 Methods

2.3.1 Initial structure generation

To generate initial structures, we started by enumerating all symmetrically unique 2Al pairs for each selected zeolite topology. The zeolite unit cells, in their pure silica form, were obtained from the international zeolite association database (IZDB),⁸⁷ and we repeated the zeolite unit cell in each direction until all cell vectors were at least 10 A. Next, for a given zeolite topology we generated supercells containing each of the possible 2Al configurations (Z_2) with Al-Al distances within 10 Å. The choice of a 10 Å cutoff distance is justified because at longer distances 2 ZCuOH is more stable than Z_2 Cu or Cu dimers (Section S5.3) for most 2Al configurations, and the % of 2Al sites populated by Z_2Cu and Cu dimers is negligible at longer (> 9.4 Å) Al-Al distances (Figure S5.1). Löwenstein's rule is the observation that Al-O-Al bond formation is unlikely to be observed in synthetic zeolites,⁸¹ and therefore Z_2 configurations with Al-O-Al were removed when enumerating 2Al configurations, except for CHA zeolite, which we kept Al-O-Al configurations for to benchmark relative Z_2Cu energies with previous work.²⁷ To determine crystallographically unique 2Al configurations, we used a connectivity-based graph isomorphism test using the python NetworkX $\operatorname{code.}^{137}$ This graph isomorphism test is a binary comparison, ¹³⁸ where all 2Al substituted zeolite unit cells connectivity of Al and Si atoms were compared to each other. The graph isomorphism test significantly reduces the number of 2Al configurations; for example, for the 36 T site CHA cell, we initially generated 630 (36 choose 2) 2Al



Figure 2.9: Initial geometry generation: (a)vector addition method and geometries generated for, (b) Z_2Cu , (c) Z_2H_2 , (d) Z_2Cu_2O , (e) $Z_2Cu_2O_2$, and (f) Z_2Cu_2OH using vector addition method. Atomic structures were visualized using the VESTA package.¹³⁹

configurations and only 25 of those 630 2Al configurations are symmetrically distinct. We also retrieve the multiplicity of each unique 2Al configuration from the isomorphism test. For example, in the 36 T site CHA unit cell, the 6MR-2NN configuration statistically occurs 36 times, and 6MR-3NN configuration only occurs 18 times. From the isomorphism test, we record these multiplicities of each 2Al configuration and the indices of Al atoms that result in the same 2Al configuration.

To generate the initial structures for mononuclear Z_2Cu , ZCuOH, and binuclear ZCuOCuZ, ZCuO₂CuZ, ZCu(OH)CuZ, and ZCu(OH)₂CuZ, we first added the extraframework species to the symmetry unique 2Al configurations in zeolite unit cells. For Z_2Cu structures, the metal ion is placed inside a zeolite ring using the vector equation:²⁷ for each unique 2Al configuration. The bold letters indicate each atom's position vectors and O_1 and O_2 are the oxygen atoms bonded to one of the Al under consideration. Figure 2.9a-b shows how this method places the Cu inside a zeolite ring on the same plane generated by Al-O₁ and Al-O₂. This method of generating initial guess Cu structures is repeated for every possible choice of bonded oxygen atoms, for example the 2Al configuration in Figure 2.9a has four oxygen associated with each Al resulting in 12 initial Cu positions. We used another graph isomorphism test to remove similar Z₂Cu structures based on the connectivity of Cu, Al, and Si in the structure, for Figure 2.9a this reduces the unique Cu locations to 6. We extended this vector addition method to generate initial structures for the species shown in Figure 2.9c-f and for ZCuOH, as discussed in Sections S1.2-S1.4, respectively.

2.3.2 High-throughput Structure Screening

The above workflow results in numerous initial guess Cu structures for each 2Al configuration and each Cu motif. For the 2Al configuration in Figure 2.9a, before symmetry reduction 12 Z_2Cu , 36 ZCuOCuZ, 36 ZCuO₂CuZ, and 36 2 ZCuOH structures are generated. For all 2Al configurations in CHA, 3000 total structures were generated, and 12,000 structures for MOR. After symmetry reduction, these numbers reduce to 2100 and 10200 for CHA and MOR, respectively. To evaluate all of these structures with DFT would be computationally expensive and likely result in many unstable high-energy structures that may fail SCF-convergence. Thus, starting from the database of structures generated through vector addition, we optimized structures using two different forcefields in series to downselect structures for spin-polarized DFT-optimizations (Scheme 2.1).

First, we performed global optimizations for all Z₂Cu, ZCuOCuZ, and ZCuO₂CuZ structures using a physics-based interatomic potential that we developed (full details provided in Section S2) to determine energy and forces, and basin hopping as the optimization algorithm^{140,141} as implemented in the Python Scipy package.¹⁴² Each structure from vector addition was input to basin hopping and we obtained the global minima computed for each structure (still 2100 total structures for CHA). Subsequently, each of these structures, along with all of the vector addition-based structures for 2 ZCuOH, was optimized to a local minimum using the FLARE¹⁴³ version 0.2.4 Gaussian process-based interatomic potentials that we trained individually for each Cu motif; full details of the method and training is in Section S3. Unlike the physics-based potential, the FLARE potential accurately predicts relative energy differences in Z_2Cu structures, but is not effective for global optimization because it lacks training data representative of structures far from local minima. The lowest energy structures computed with FLARE for each Cu motif at a given 2Al configuration were then used as input structures for subsequent DFT calculations; additional structure selection details are reported in Section S3. For example, we optimized 6 symmetry distinct CHA-Z₂Cu structures using the physics-based potential followed by the FLARE potential, and then picked the two lowest energy structures of the six for subsequent optimization with DFT. To downselect Cu dimer species, we checked the connectivity of each extraframework Cu motif and the zeolite framework. For example, in Z_2Cu_2O , we checked if Cu-O-Cu bonds were preserved, and no Si-O or Al-O bonds were broken in the zeolite framework. If either of these were violated the structure was discarded. Altogether, filtering structures using this approach resulted in a significant reduction (3,000 to 190 for CHA and 12,000 to 640 for MOR) in the number of initial guess structures for DFT calculations. We emphasize that all of the results reported in Results and Discussion use only DFT-computed energies.



Scheme 2.1: Workflow for generating structures for DFT calculations. Initial structure generation, sequentially optimized using the physics-based force field and machine learning potential. Finally, DFT calculations are used for exchange energy evaluations.

We predicted the minimum energy Z_2H_2 structures for each 2Al configuration using the ZH energies computed for each symmetry unique T site and structural descriptors of vector addition-generated Z_2H_2 structures. Our model for predicting relative energies of Z_2H_2 structures (details in Section 4.3) is based on DFT calculations reported by Nystrom et. al,¹⁴⁴ where we use Al-Al and H-H distances evaluated before DFT-geometry optimization to estimate the relative energy of Z_2H_2 . From this screening we acquired the lowest energy Z_2H_2 structure for each unique 2Al site, and then used DFT to optimize and obtain the energy of the selected Z_2H_2 structure. This method results in significant downsampling to approximately one structure input to DFT for every 16 Z_2H_2 structures generated.

We calculated the energies of all 2ZCuOH structures generated for CHA and MOR using DFT, and our results suggest that if Al-Al separation distances are > 10 Å, the energy of exchanging Cu into two isolated ZH motifs to form 2ZCuOH is approximately equal to the energy of exchanging 2Cu at Z_2H_2 to form 2 ZCuOH structures. Full details are reported in Section 4.4. Therefore, past 10 Å, we approximated 2 ZCuOH exchange energies with 2× ZCuOH exchange free energies. For AFX, BEA, and FER we used these mean-field 2 ZCuOH energies computed for each T site pair instead of computing 2 ZCuOH energies separately for each 2Al. The majority of ZCuOH structures optimize to threefold coordinated Cu centers, however, a minority of sites form fourfold coordinated ZCuOH (with three bonds to extraframework oxygen), consistent with previously reported structures.¹⁴⁵

2.3.3 DFT calculations and exchange free energies

To compute Cu exchange free energies ($\Delta G_{\text{species}}$) at each 2Al configuration, we optimized all the Z_2H_2 , Cu monomer, and Cu dimer structures (selected from our structure screening described above) using the Vienna Ab Initio Simulation Pack age^{146} (version 5.4.4). Structures files for optimized structures are provided as a supplementary attachment. Our spin-polarized DFT calculations used the projectoraugmented wave^{146,147} method of core valence interactions and a plane wave cutoff energy of 400 eV. The first Brillouin zone was sampled at the Γ point only, as appropriate for the large supercells (cell vectors for all zeolites multiplied until > 10Å) of these insulators. The generalized gradient approximation functional of Perdew-Burke-Ernzerhof (PBE)¹⁴⁸ was used to describe the exchange-correlation potential with the Becke-Johnson damping method (D3(BJ)vdw) included for dispersion corrections.^{149,150} Motivated by recent literature reports,¹⁵¹ and limitations in the accuracy of energies for some Cu-ion complexes computed using DFT,^{62,151–153} we also tested the sensitivity of our predictions to PBE+U (Section S5.4) with a U parameter calibrated with crystalline Cu dimer compounds.¹⁵¹ All electronic energies were converged to 10^{-6} eV and atomic forces to less than 0.03 eV/Å. Harmonic vibrational frequencies were computed with finite differences on atomic forces with displacements of 0.015 Å for all the atoms. Zero point vibrational energies (ZPE) were computed as:

$$ZPE = \sum_{i} \frac{1}{2} h v_i \tag{2.12}$$

To calculate the vibrational entropy of each dimeric and monomeric species $(Z_2Cu_xO_yH_z(s))$, we included frequencies > 100 cm⁻¹, and frequencies < 100 cm⁻¹ were set to 100 cm⁻¹.¹⁵⁴

$$S_{\text{vib.}} = -k_{\text{B}} \sum_{i} \ln\left(1 - e^{-\frac{hv_i}{k_{\text{B}}T}}\right)$$
(2.13)

To compute the exchange free energy of species ($\Delta G_{\text{species}}$), we used eqn. 2.1 and the DFT-computed (including ZPE's for all species) exchange reaction energy ($\Delta E_{x,y,z}$) computed as follows:

$$\Delta E_{x,y,z} = E_{Z_2 Cu_x O_y H_z(s)} - E_{Z_2 H_2(s)} - x E_{CuO(s)} - \frac{(2y - 2x - z + 2)}{4} E_{O_2(g)} - \frac{(z - 2)}{2} E_{H_2 O(g)}$$
(2.14)

Treating the system as closed with respect to the Cu concentration gives the free energy as:

$$\Delta G_{x,y,z} = \Delta E_{x,y,z} + \Delta \text{ZPE}_{x,y,z} - T \Delta S_{\text{vib.}(x,y,z)} - x \Delta G_{\text{CuO}}(T) - \frac{(2y - 2x - z + 2)}{4} \Delta \mu_{\text{O}_2(g)}(T, P_{\text{O}_2}) - \frac{(z - 2)}{2} \Delta \mu_{\text{H}_2\text{O}(g)}(T, P_{\text{H}_2\text{O}})$$
(2.15)

where the chemical potentials $\Delta \mu_i$ of gas species and free energy of CuO ($\Delta G_{CuO}(T)$) are evaluated as follows:

$$\Delta \mu_i = (G^{\rm o}(T) - G^{\rm o}(0 \text{ K})) + k_{\rm B}T \ln\left(\frac{P}{P^{\rm o}}\right)$$
(2.16)

$$\Delta G_{\rm CuO}(T) = G^{\rm o}(T) - G^{\rm o}(0 \text{ K})$$
(2.17)

using free energy values interpolated from the NIST JANAF thermochemical tables.¹⁵⁵

To avoid many computationally expensive frequency calculations we assumed $\Delta \text{ZPE}_{x,y,z}$ and $S_{\text{vib.}(x,y,z)}$ are independent of 2Al configuration and zeolite topology, and depend only on the specific Cu motif. To estimate the ZPE and $S_{\text{vib.}}$ corresponding to each Cu motif a number of structures were sampled, these results show minimal variation for a given Cu motif and were averaged for use on other 2Al configurations (Section S5). Based on these calculations, we expect the errors introduced by assuming such 2Al configuration independence is negligible compared to the other terms such as $\Delta E_{x,y,z}$. The CuO(s) formation energy:

$$Cu(s) + \frac{1}{2}O_2(g) \longrightarrow CuO(s)$$
 (2.18)

is incorrectly predicted by the PBE (-131 kJ mol⁻¹) functional, and therefore, we corrected the energy of CuO such that it reproduces the experimentally reported formation enthalpy (-154 kJ mol⁻¹).¹⁵⁵ However, we did not apply this correction to our PBE+U calculations (Section S5.4), because the PBE+U functional more accurately predicted the CuO formation enthalpy (-152 kJ mol⁻¹). We compared exchange free energies obtained from PBE with PBE+U (with $U = 6 \text{ eV}^{151}$ and all other parameters kept the same as PBE), and observed only minor changes in relative exchange free energies between the Cu motifs as shown in Section S5.4.

2.3.4 Monte Carlo Simulations

To estimate the equilibrium fraction of different Cu species in a macroscopic zeolite system, we used Monte Carlo (MC) simulations based on the computed Cu exchange probabilities for each species at all 2Al sites in the corresponding zeolite supercell. The zeolite supercells used for our DFT calculations were repeated 3x3x3 times to improve the sampling of 2Al configurations.

For a given Si:Al ratio we generated a $3 \times 3 \times 3$ zeolite supercell and populated with Al up to the desired ratio, according to the rules described below. Subsequently, every possible 2Al configuration in the cell is enumerated, and relative probabilities for exchange of each of the six Cu motifs for each 2Al configuration are computed (eq. 2.19).

$$p_{i,s} = \frac{\exp\left(\frac{-\Delta G_{i,s}}{RT}\right)}{\sum_{i=1}^{N_{2Al \text{ config.}}} \sum_{s}^{\text{All Cu species}} \exp\left(\frac{-\Delta G_{i,s}}{RT}\right)} .$$
(2.19)

These probabilities are used to generate a weighted list of all possible Cu exchange events and a random number between 0-1 is chosen to select the exchange event, then the identity of Cu species and the 2Al configuration populated is recorded. Once a 2Al site is occupied by a dimer or monomer, we remove that Al pair from our 2Al list, generate a new probability list, and repeat the Cu exchange until all the 2Al sites in the zeolite are exhausted. For each Si:Al ratio, we averaged 20,000 independent MC simulations and created 1-D interpolations of the occupied Cu fraction as a function of Cu:Al for each species. Subsequently, all the 1-D interpolations for Si:Al=3-55 were combined to generate the 2-D interpolations of species shown in Figure 2.3. We verified the convergence of our MC simulations by executing a separate MC simulation with 10,000 2Al configurations (Section S8).

When populating Al for our MC simulations, we excluded the 1NN 2Al configurations (Al-O-Al), obeying Löwenstein's rule.⁸¹ Otherwise, each Al is populated randomly or follows a T site bias according to the required macroscopic T site occupancy by Al (Section S8.1). Sample code for the MC simulations has been provided as a supplementary attachment file.

2.3.5 Binary classification model for predicting dimer formation

To identify the 2Al configurations for a given topology that favor Cu exchange as dimers, we trained an XGBoost¹⁵⁶ decision tree classification model. Based on the dimer formation probabilities $(p_{i,s})$ at Cu exchange conditions of 10⁻⁶ kPa H₂O, 20 % O₂ at 973 K, calculated using equation 2.5, we labeled all 2Al configurations in CHA, MOR, AFX, and BEA as 1 $(p_{i,s} \ge 0.5)$ or 0 $(p_{i,s} < 0.5)$. To generate the structural descriptors for the model, we used the Atomic Simulation Environment (ASE)¹⁵⁷ and NetworkX¹³⁷ python packages. For all unique 2Al configurations, Al-Al distances (in Å) in unoptimized zeolite cells and the nearest neighbor connectivity's (integer, refer to Section S11.1 for details) were generated as the first set of descriptors for the classification model.

We generated the second set of descriptors using random sphere packing to improve the classification accuracy. We sample the zeolite void space by randomly placing points in the zeolite unit cell with an average density of 1 point Å⁻³. Then, we removed all points within 2.0 Å of framework atoms, thereby only retaining points that fill the zeolite void space (Figure S11.1). This 2.0 Å cutoff was chosen to capture Cu-framework oxygen interactions where Cu-O bonds are ≈ 1.95 Å.^{27,60} We derived a custom descriptor, "projected void space" defined as:

Projected void space =
$$\sum_{\text{mid(Al-Al) to sphere distance (d)}}^{\text{All random spheres retained}} e^{(-\alpha d)}$$
(2.20)

to capture the nature of the random packing, where d is the distance measured from the bisection point of Al-Al to all the random spheres retained, and α is a hyperparameter for the projection. Additional details and figures for this approach are located in Section S11.1. Statistics (minimum, maximum, average, and standard deviation) of the projected void space were generated from 2000 independent random sphere packing simulations for each 2Al configuration. Al-Al distance, nearest neighbor connectivity, and statistics of random sphere packing were used as features in our classification model. Therefore, our training dataset consists of six descriptors and 318 data points (CHA-21, MOR-100, BEA-154, AFX-43), and FER data was held out as a validation set.

We used the XGBoost classifier as implemented in the open source Python code from Chen *et al.*¹⁵⁸ because boosting tree algorithms have proven robust for small data sets.^{159,160} The hyperparameters of the XGBoost model and α in void space projection were optimized using grid searches (Section S11). The 10-fold cross-validation accuracy of the model was used as the metric for comparing different models. More details on hyperparameter optimization and model accuracy can be found in Section S11. The training data set has more 2Al sites that favor monomer formation (69.5% of 2Al) than dimers (30.5% of 2Al), indicating a mild class imbalance. Therefore, we tested ML models with and without adjusting for class imbalance (Section 11.3) and found similar performance for both models.

To identify the features that are the most important when deciding a 2Al configuration's dimer (or monomer) preference, we used the "feature importance score", defined as how many times a feature is selected for splitting (making a decision), weighted by the squared improvement of the model gained by each split, and averaged over all trees.^{161,162} The final XGBoost model is provided as a supplementary attachment file.

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Supplementary Info: ZIP file containing DFT-optimized structure files with their DFT-computed energies and exchange free energies, sample Python codes for MLP training and optimized parameters for physics-based forcefield, and a sample code for MC simulations are available, and optimized XGBoost model.

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Chapter 3

Kinetic and Thermodynamic Factors Influencing Palladium Nano-particle Redispersion into Mononuclear Pd(II) Cations in Zeolite Supports

This chapter has been reproduced in its entirety with permission from Lardinois, T. M.; Mandal, K.; Yadav, V.; Wijerathne, A.; Bolton, B. K.; Lippie, H.; Li, C. W.; Paolucci, C., and Gounder, R. J. Phys. Chem. C 2022, 126, 19, 8337– 8353. Copyright 2020 American Chemical Society. The supplementary materials for this paper/ chapter are available on https://doi.org/10.1021/acs.jpcc.2c01613. This chapter studies the interconversion between Pd nanoparticles and cations in Pd-CHA (SSZ-13) zeolites. These processes are responsible for the thermal activation and deactivation of Pd-CHA materials and provide routes for catalyst regeneration. I contributed to the kinetic analysis of this study by (1) combining the Ostwald ripening model with an atom trapping reaction to simulate the particle redispersion process and (2) performing kinetic Monte Carlo simulations to solve the resulting large system of differential equations. I also regressed the kinetic parameters to the experimental redispersion data to estimate model parameters. As a coauthor on the paper, I was responsible for writing the methods section for the kinetics model.

3.1 Introduction

The dynamic processes responsible for the sintering of metal nanoparticles and their redispersion into smaller clusters and isolated atoms and ions on oxide supports strongly influence the reactivity, selectivity, deactivation, and regeneration of heterogeneous catalysts and adsorbent materials.^{1–6} The redispersion of nanoparticles and clusters to single atoms results in catalyst deactivation for methane oxidation on Pd supported on $Al_2O_3^7$ and Pt supported on CeO_2^8 NO reduction in the presence of CO on Pt supported on aluminosilicate MWW zeolites,^{9,10} CO oxidation on various metals (Ru,¹¹ Rh,¹¹ Ir,¹¹ Pt,¹² and Pd¹³) supported on CeO₂, and propane dehydrogenation on Pt-Sn clusters supported on CeO_2 .¹⁴ Conversely, the formation of metal nanoparticles from single atoms causes deactivation of Pt,^{8,15} Pd,^{11,15} Cu,¹⁶ and Rh¹⁵ on CeO_2 for CO oxidation, Au on $CeZrO_4^{17}$ and CeO_2^{18} for the water-gas shift reaction, Au on carbon for acetylene hydrochlorination,^{19,20} and Rh on aluminosilicate zeolites or TiO_2 for methane oxidation to methanol.²¹ Compared to catalysts containing larger nanoparticles, catalysts composed of single atoms and sub-nanometer sized clusters are typically more susceptible to structural changes in response to their reaction environment, and thus tend to sinter more readily via Ostwald ripening (OR) under reducing conditions at high temperatures.^{1,22} Redispersion of nanoparticles to single atoms and ions can facilitate catalyst regeneration;^{23,24} however, the atomistic details of the thermodynamic driving forces and kinetic mechanisms governing such redispersion processes are not well-understood.

The structural interconversion between oxide-supported Pd nanoparticles and cations is strongly affected by reaction conditions and nanoparticle sizes,^{7,10,25–32} and is of particular relevance for several catalytic and adsorption applications including CO oxidation,^{11,13,33–35} Wacker oxidation,^{36–38} methane oxidation,^{39–43} alkene hydrogena-tion, $^{44-47}$ and low-temperature (<473 K) NO trapping in diesel engine emissions.^{48–52} While the dominant active sites for methane oxidation are located on Pd nanoparticles,^{7,53} isolated Pd atoms and cations are the active sites for Wacker^{36–38} and CO oxidation,⁵⁴ hydrodechlorination,⁵⁵ and NO trapping in passive NOx adsorber materials.^{56,57} The redispersion of Pd nanoparticles to cations is facilitated by reactants such as NO (during NOx reduction on TiO_2 -supported three-way catalysts,⁵⁸ H₂-selective catalytic reduction of NO on ZrO₂ supports,⁵⁹ sequential adsorption of CO and NO on ceria-zirconia supports,⁶⁰ and solid-state ion-exchange in CHA zeolites⁶¹) and water (in FAU zeolites during Wacker oxidation³⁶⁻³⁸), and via hydrothermal treatments with steam and air in aluminosilicate MFI, MWW and CHA zeolites.^{62–64} Redispersion can be further promoted when synthesis protocols are used that promote the formation of defect or cation-exchange sites in the support that are able to capture mobile metal species emitted from nanoparticles in atom trapping processes.^{23,24} Metal-support interactions also play a crucial role to stabilize dispersed isolated atoms, with CeO₂ and Fe₂O₃ supports exhibiting strong binding to Pt,^{12,14,15,65,66} Rh,¹⁵ Ru,⁶⁷ and Cu.^{6,16} Despite the low vapor pressure of Pd,¹⁵ atom trapping mechanisms have been shown to stabilize isolated Pd on CeO_2 ,^{11,15,55,68} TiO_2 ,⁶⁹ γ -Al₂O₃,^{7,54} and aluminosilicate zeolites. Yet, numerous questions regarding the kinetic and thermodynamic factors that influence conversion of Pd nanoparticles to single atoms and cations, and their dependence on reaction conditions, initial Pd particle size, and the metal-support interaction remain unanswered.

In this work, we examine the thermodynamic and kinetic factors and reaction mechanisms that govern the interconversion of Pd nanoparticles and cations, studying Pd supported on aluminosilicate zeolites, given that these concepts are particularly relevant for Pd-exchanged zeolites being explored in practical applications as materials for passive NOx adsorption (PNA)^{50,56,57} in automotive exhaust, Wacker^{36–38} and methane oxidation.^{39,68,70,71} Zeolite supports are also a versatile materials platform for performing fundamental experimental studies because of the structural uniformity of their crystalline frameworks and the ability to synthesize them with precise modifications in bulk and atomic composition, which enable more faithful comparisons to the structures modeled by theoretical studies. Pd-zeolites typically contain various Pd structures^{64,72} of different nuclearity (mono- and polynuclear)^{56,73,74} and valence (zero- to tetravalent),^{75–79} but only extraframework, mononuclear cation sites chargecompensated by framework Al atoms (ion-exchanged Pd) are the purported binding sites for NOx adsorption in the context of PNA applications⁸⁰ and the active sites for Wacker oxidation.^{36–38} The structural lability of Pd allows interconversion between agglomerated domains and mononuclear ion-exchanged sites,⁸¹ which depends on the size of Pd nanoparticle domain sizes and their density on the support,⁷ and causes undesirable agglomeration and deactivation under PNA and Wacker-relevant conditions.^{57,62,82,83} Yet, such structural lability allows for the redispersion of agglomerated domains to ion-exchanged sites under high-temperature (>500 K) air⁸⁴ or $NO^{61,85}$ regeneration. Together, these challenges and observations motivate improved fundamental understanding of the critical thermodynamic and kinetic factors that govern Pd structural interconversion in zeolites, to guide the design of these materials and regeneration protocols based on solid-state ion-exchange routes.

Here, we combine experiment and theory to understand the influence of initial Pd nanoparticle size and external gas conditions on the thermodynamic and kinetic factors influencing structural conversion between Pd nanoparticles and ionexchanged Pd^{2+} in CHA zeolites. Pd-CHA zeolites are prepared to initially contain normally-distributed or log-normally distributed Pd particles of different mean size, located at extracrystalline zeolite surfaces. These materials are then treated to high temperatures (598–973 K) in flowing air with and without H_2O , and the number of agglomerated PdO domains and ion-exchanged Pd^{2+} sites are quantified with H_2 temperature-programmed reduction (TPR). Density functional theory (DFT) computed thermodynamic phase diagrams are constructed for a range of Pd particle sizes under various gas environments (P_{O_2} , P_{H_2O} , temperature) to quantitatively compare with experimentally measured ion-exchanged Pd^{2+} contents on samples exposed to similar treatments to show that H₂O can promote the formation of PdO agglomerates from Pd^{2+} cations. Apparent rates of conversion of metallic Pd domains to ion-exchanged Pd²⁺ sites under flowing air are measured as a function of temperature (598-673 K) and H₂O pressure (0-2 kPa) to deduce mechanistic information and determine kinetic implications of H₂O and O₂ pressures and the Pd particle size on the redispersion to ion-exchanged Pd²⁺ sites. Kinetic Monte Carlo (kMC) simulations are performed to rationalize the observed kinetics, and show that Pd redispersion at temperatures <900 K does not occur through a gas-phase process, but rather through a surface-mediated OR mechanism whereby mobile monomers diffuse on the zeolite support and bind at ion-trapping sites.

3.2 Methods

3.2.1 Pd-Zeolite Characterization

The amounts of agglomerated PdO and mononuclear Pd²⁺ cations were quantified with H_2 TPR procedures described elsewhere⁸⁴ using a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a thermal conductivity detector (TCD) to quantify H_2 consumption. In brief, the TCD response factor was generated using varied partial pressures (0.5-5.0 kPa) of H₂ in balance Ar, which quantified the amount of Ag on a Ag_2O reference material (Micromeritics) to within a factor of 1.12. After a given treatment sequence, samples (0.3-0.6 g) were exposed to flowing Ar $(0.50 \text{ cm}^3 \text{ s}^{-1}, \text{ UHP}, 99.999\%, \text{ Indiana Oxygen})$ with 1–2 kPa H₂O for >0.5 h to hydrate mononuclear Pd^{2+} cations at 303 K. Samples were then cooled to 203 K (0.167 K s⁻¹) in flowing Ar (0.167 cm³ s⁻¹) using a Micromeritics Cryocooler II accessory. An isopropanol slurry (cooled to 184 K with liquid N_2) was inserted between the TCD detector and the sample to trap any condensable gases. The Ar stream was replaced with 5 kPa H_2 in balance Ar (0.167 cm³ s⁻¹, certified mixture, Indiana Oxygen), and once a stable TCD signal was achieved, the sample was treated to 573 K (0.167 K s⁻¹) and held for 0.5 h. All H_2 TPR profiles and discussion of data fitting procedures are reported in Section S4, SI.

Volumetric O₂ chemisorption experiments were performed with a Micromeritics ASAP 2020 Plus Chemisorption unit. Samples (~0.2 g) were treated in flowing H₂ (UHP, 99.999%, Praxair) to 673 K or 873 K in O₂ (UHP, 99.98%, Matheson) before preparing for chemisorption. Samples were first flushed in flowing He then degassed under vacuum (< 3 mHg) for 1 h at 373 K. Next, a leak test was performed to confirm that leak rates were below the threshold of < 600 mHg h⁻¹ (recommended by Micromeritics). Samples were then treated in H_2 to 573 K (0.167 K s⁻¹) for 1 h, evacuated at 573 K for 1 h, then another leak test was performed at 313 K. Then, the sample was evacuated for 0.3 h at 313 K before collecting two O₂ adsorption isotherms (313 K, 2–42 kPa), with an evacuation step after the first isotherm to remove non-chemisorbed O₂. Isothermal uptakes were linearly extrapolated to zero pressure, and the difference in uptakes at zero partial pressure yielded the amount of chemisorbed O₂. The dispersion was calculated assuming one O atom titrates one surface Pd atom.

3.2.2 Isothermal Pd Redispersion Kinetics.

The as-exchanged $[Pd(NH_3)_4]^{2+}$ -CHA (2.2 wt% Pd) material was first pelleted then sieved to retain 180–250 μ m diameter aggregates. Treatment sequences and H₂ TPR analysis were performed with a Micromeritics Autochem II 2920 Chemisorption Analyzer. Samples (0.03–0.05 g) were first pretreated in flowing H₂ in Ar (0.5 cm³ s⁻¹; 5 kPa H₂, certified mixture, Indiana Oxygen) to 673 K for 1 h, and cooled to ambient temperature. Samples were then cycled through H₂ treatments, inert purge treatments, air treatments (i.e., isothermal redispersion treatments), and then the amounts of PdO and Pd²⁺ cations were quantified by H₂ TPR. As an example procedure for an isothermal redispersion measurement at 648 K in air without added H₂O, the sample was treated in flowing (0.5 cm³ s⁻¹) 5 kPa H₂ in Ar to 648 K (0.167 K s⁻¹) for 0.5 h, then the 5 kPa H₂ in Ar stream was replaced with flowing Ar (0.5 cm³ s⁻¹; UHP, 99.999%, Indiana Oxygen) to purge the system for 0.083 h. Then, the Ar stream was replaced with flowing air (0.5 cm³ s⁻¹; Air Zero, Indiana Oxygen) for a specified amount of time (0.003–1 h), and then rapidly cooled (0.67 K s⁻¹) from 648 K to ambient temperature in flowing Ar (0.5 cm³ s⁻¹) Ar using a Micromeritics Cryocooler II accessory. In cycling experiments, the air exposure times were randomly varied between 0.003–1 h to avoid any systematic errors that may have been caused by this step in the procedure.

3.2.3 Details of DFT, and Ab Initio Formation Free Energies Calculations.

We used the Vienna ab initio simulation package (VASP, version 5.4.4)⁸⁶ to perform plane-wave, periodic DFT calculations with an energy cutoff of 400 eV and projected augmented wave (PAW)⁸⁷ pseudopotentials for core-valence interactions. We used the bulk structures reported in the Materials Project⁸⁸ database for metallic Pd and PdO, and the 24 T-site 1Al and 2Al Pd-exchanged SSZ13 species in the study by Mandal et al.⁸⁹ as initial guesses, and optimized them with the Perdew-Becke-Ernzerhof (PBE)⁹⁰ functional and subsequently, the Heyd-Scuseria-Erzenhof (HSE06)^{86,90–96} hybrid exchange-correlation functional. Dispersion corrections were calculated using the Becke-Johnson damping (D3(BJ)-vdw) method.^{91,92} We used the HSE06 functional with D3(BJ) dispersion corrections because it correctly captures the formation energy of PdO within 2 kJ mol⁻¹ of the experimental value (Table S5.2, SI). We used a convergence threshold of 10^{-8} eV and 0.01 eV/Å for the electronic energies and atomic forces, respectively. We used the Monkhorst-Pack k-point mesh detailed in the Materials Project database to sample the first Brillouin zone for bulk metallic Pd and PdO; only the Γ point was used for zeolitic structures. The optimized geometries of 6-MR 3NN Z_2H_2 and Z_2Pd have been provided in the CONTCARS attachment of the SI. Additional details about the formation energy calculations can be found in Section S5, SI.

3.2.4 Details of Particle Size Dependent Models.

To estimate surface energies, we used the Python Materials Genomics (*Pymatgen*) package and its built-in *Slabgenerator* function^{97–99} to construct symmetric slabs of up to Miller index 2 for metallic Pd and PdO from their respective optimized bulk structures. The slab thickness was set to 10 Å, and a 15 Å vacuum space was applied to eliminate interactions between the periodic images of the surfaces in the z direction. The k-point mesh for the slabs in the x and y directions was appropriately scaled by using the k-points per reciprocal Å for the bulk structures, with a single k-point applied in the z direction. We optimized and computed the energies of the unconstrained slabs using the PBE-D3(BJ)-vdw functional due to computational expense, and the same convergence criteria as that for the bulk structures. The surface energies (γ_{stab}) of the slabs were calculated as:¹⁰⁰

$$\gamma_{\rm slab}(P_{\rm O_2}, \ T) = \frac{E_{\rm slab} - n_{\rm Pd}E_{\rm bulk} - n_{\rm O}\mu_{\rm O}(P_{\rm O_2}, \ T)}{2A}$$
(3.1)

where $n_{\rm Pd}$ and $n_{\rm O}$ represent the number of Pd atoms and excess or deficit O atoms in the slab, respectively, $\mu_{\rm O}$ is the chemical potential of O, A denotes the surface area of one side of the slab, $E_{\rm slab}$ and $E_{\rm bulk}$ are the total energy of the slab and the energy of the bulk per formula unit, respectively. The equilibrium shapes of metallic Pd and PdO nanoparticles were determined from their respective Wulff constructions which represent the minimum surface energy for a given crystal. We used the *Wulffshape* function in *Pymatgen* to generate the Wulff constructions for a range of μ_O values,¹⁰¹ and evaluated the average surface energy (γ).

Based on data fitted to calorimetric measurements of the chemical potentials of transition metals on oxide supports, Campbell et al.^{102–104} expressed the free energy

of supported hemispherical nanoparticles of an effective diameter d relative to bulk (ΔG) as follows:

$$\Delta G(d, P_{O_2}, T) = (3\gamma (P_{O_2}, T) - E_{adh}) \left(1 + \frac{1.5}{d}\right) \left(\frac{2\rho}{d}\right)$$
(3.2)

where ρ represents the volume normalized per mole of metal. The adhesion energy between the nanoparticle and the support E_{adh} is expressed according to the Young equation:

$$E_{\rm adh} = \gamma (1 + \cos \theta) \tag{3.3}$$

where θ is the contact angle between the particle and support. While $\theta = 66 - 90^{\circ}$ has been reported for Pd on SiO₂,^{105,106} it is unknown for PdO on SiO₂; therefore, we considered multiple values of $\theta = 60^{\circ}, 90^{\circ}$, and 120° which are representative of varying degrees of adhesion (Figures S5.9-10, SI).

Subsequently, we evaluated the formation free energy of PdO nanoparticles $(\Delta G_{\text{PdO}}^{\text{form}})$ by incorporating the size-dependent free energy of PdO nanoparticles (ΔG_{PdO}) with respect to bulk Pd (Eq. 3.2) as:

$$\Delta G_{\rm PdO}^{\rm form}\left(d_{\rm PdO}, P_{\rm O_2}, T\right) = \Delta G_{\rm PdO_{\rm bulk}}^{\rm form}\left(P_{\rm O_2}, T\right) + \Delta G_{\rm PdO}\left(d_{\rm PdO}, P_{\rm O_2}, T\right) - \Delta G_{\rm Pd}\left(d_{\rm Pd}\right)$$

$$(3.4)$$

To relate the increment in volume associated with the formation of PdO from Pd, we used the ratio of the particle diameters of PdO and Pd ($d_{PdO}/d_{Pd} = 1.19$) from the reported densities of bulk Pd ($\rho_{Pd} = 11.41 \text{ g cm}^{-3}$) and PdO ($\rho_{PdO} = 7.79 \text{ g cm}^{-3}$).⁸⁸

3.3 Results

3.3.1 Effects of Initial Pd Particle Size and Treatment Conditions on the Conversion of Agglomerated Pd Particles to Exchanged Pd²⁺ ions

3.3.1.1 Synthesis of Monodisperse Pd Nanoparticles Supported on CHA Zeolites

To isolate the effects of Pd particle size on their structural interconversion to mononuclear Pd^{2+} cations that are charge-compensated by framework Al in zeolite supports (denoted "ion-exchanged Pd^{2+} ") during high-temperature air treatments, Pd particles of monodisperse size distributions were synthesized using solution-phase colloidal synthesis methods⁷ and then deposited onto the exterior of CHA zeolite crystallites (details of Pd deposition procedures in Section S1, SI). Three different colloidal Pd nanoparticle solutions were characterized with TEM to contain monodisperse particles that were nominally 2, 7, and 14 nm in diameter (Figures S2.3–S2.6, SI). These colloidal solutions were diluted in a hexane solvent and mixed with the H-form CHA zeolite powder, and then sonicated to deposit the oleylamine-capped Pd particles (denoted "as-deposited Pd-CHA"). Samples are referred to as Pd-CHA-X-ND, where X is the average particle diameter (in nm) on as-deposited samples and where the suffix ND denotes that a normal distribution of particle sizes are present initially, as determined by TEM.

Figure 3.1 shows *ex situ* TEM images of the as-deposited Pd-CHA-X-ND samples, and **Table 3.1** lists their particle size distributions and elemental analysis. Pd particle size distributions were similar on as-deposited Pd-CHA-X-ND samples as in



Figure 3.1: *Ex situ* TEM images of the as-deposited Pd-CHA-X-ND materials: Pd-CHA-2-ND (left), Pd-CHA-7-ND (middle), Pd-CHA-14-ND (right).

Table 3.1:	Characterization	Data	on	As-deposited	Pd-CHA-X-ND
$Samples^a$					

	nominal Pd	TEM characterized		
$sample^{b}$	particle size / nm $$	particle size / nm^c	Pd wt $\%^d$	$\mathrm{Pd}/\mathrm{Al}^d$
Pd-CHA-2-ND	2	2.2 ± 0.5	1.12	0.082
Pd-CHA-7-ND	7	6.8 ± 0.7	0.72	0.053
Pd-CHA-14-ND	14	14.4 ± 1.6	0.84	0.061

^{*a*}Particle size distributions are reported in Figure S2.7–2.9, Supporting Information. ^{*b*} Samples are denoted as Pd-CHA-X-ND, where X denotes the nominal Pd particle size and ND denotes a normal particle size distribution. ^{*c*} The average particle size plus or minus one standard deviation. ^{*d*} The Pd wt % and Pd/Al molar ratio were determined by inductively coupled plasma (ICP) spectroscopy.

the colloidal precursor solutions, demonstrating the deposition procedure used did not alter the monodisperse distributions of olevlamine-capped Pd nanoparticles; however, this deposition procedure did result in some non-uniformities in how Pd particles were spatially distributed at external crystallite surfaces, with some localized Pd nanoparticle aggregation observed for the Pd-CHA-7-ND and Pd-CHA-14-ND samples. To remove organic species without altering the Pd particle size distribution, as-deposited Pd-CHA-X-ND samples were first treated in air to 548 K for 4 h, before studying the effects of higher temperature air treatments. Samples treated with this protocol were analyzed in a subsequent TGA experiment and did not show desorption events for organic species (460–600 K), and TGA profiles were similar to that of the parent H-CHA support (Figures S3.1 and S3.2, SI), indicating that the majority of organic content at exterior Pd surfaces was successfully removed. TEM images of Pd-CHA-X-ND samples treated to 548 K in air showed similar Pd particle size distributions as present in their as-deposited form (Figures S2.10–S2.13, SI). Therefore, we conclude that treatment of as-deposited Pd-CHA-X-ND samples in air to 548 K successfully removed the majority of organic species while retaining the Pd particle size distribution and zeolite support intact, enabling subsequent studies of the conversion of such particles to Pd^{2+} cations upon treatment to higher temperatures (>548 K).

3.3.1.2 Effects of Pd Particle Size on Pd Oxidation and Structural Interconversion

The as-deposited Pd-CHA-X-ND samples were treated to high temperatures (598– 873 K) in flowing air to determine the effects of Pd particle size on the extent of oxidation with O_2 and conversion to Pd^{2+} cations. The amounts of agglomerated PdO domains and Pd^{2+} cations after high-temperature air treatments were charac-



Figure 3.2: (a) The amount of ion-exchanged Pd^{2+} (per total Pd) after treatment in flowing air (593 873 K) for Pd-CHA-2-ND (squares), Pd-CHA-7-ND (circles), and Pd-CHA-14-ND (triangles). (b) Total H₂ consumed (per total Pd) from (a). Dashed lines represent theoretical maximum amounts. H₂ TPR profiles reported in Figures S4.1 S4.3, SI.

terized with H_2 TPR (profiles reported in Figures S4.1–S4.3, SI). Previous reports concluded that agglomerated PdO domains have a lower barrier for reduction by H_2 than hydrated Pd²⁺ ion sites; thus, H_2 consumption features can be quantified and assigned to agglomerated PdO and ion-exchanged Pd²⁺ (further discussed in Section S4, SI).^{81,84,107,108}

The total H₂ consumption (per total Pd) and the amount of ion-exchanged Pd²⁺ (per total Pd) after treatment in flowing air Pd-CHA-X-ND samples are reported in **Figure 3.2**. At a given air treatment temperature, the amount of ion-exchanged Pd²⁺ formed on CHA increased as the initial Pd nanoparticle size decreased, consistent with previous reports that smaller Pd nanoparticles (at fixed Pd density) were converted to greater amounts of mononuclear Pd(OH)₂ on γ -Al₂O₃.⁷ For Pd-CHA-2-



Figure 3.3: (a) Framework of chabazite (CHA) made up of four-, six-, and eightmembered rings (MR). (b) Pd cations exchanged at 1Al and 2Al sites.

ND, the total H₂ consumed per Pd was near unity at all air treatment temperatures studied; thus, all of the 2 nm Pd nanoparticles were oxidized to Pd²⁺ during the air treatment. In contrast, Pd-CHA-7-ND and Pd-CHA-14-ND showed sub-unity H₂ consumption per Pd for low-temperature air treatments (598–673 K), suggesting that a fraction of the 7 nm or 14 nm Pd nanoparticles were not fully oxidized during the air treatment, consistent with a report by Chin et al. showing that higher O₂ pressures were needed to fully oxidize larger metallic Pd particles supported on γ -Al₂O₃ at a fixed temperature of 973 K.¹⁰⁹

3.3.1.3 Thermodynamics of Conversion of Agglomerated Pd Particles to Exchanged Pd²⁺ Ions

Estimating the maximum fraction of Pd atoms in nanoparticles that can convert to ion-exchanged Pd^{2+} based on thermodynamic considerations requires calculation of both nanoparticle and ion-exchanged zeolite energies. Previous studies have shown that Pd^{2+} cations charge-compensating two Al tetrahedral sites (2Al) in the sixmembered ring (6-MR) are the most thermodynamically stable ion-exchanged Pd^{2+}

Table 3.2: HSE06-D3(BJ)vdw-calculated 0 K Formation Energies (ΔE), and Formation Free Energies of Bulk PdO ($\Delta G_{PdO_{bulk}}^{form}$), and 3NN Z₂Pd ($\Delta G_{Z_2Pd}^{form}$) at 598 K and 873 K, 20 kPa O₂, 0.014 kPa H₂O.

		$\Delta {\rm G}^{\rm form}$ kJ (mol Pd) ⁻¹	
reaction	$\Delta E~kJ~(mol~Pd)^{\text{-1}}$	598 K	873 K
$\mathrm{Pd}_{\mathrm{bulk}} + \frac{1}{2}\mathrm{O}_2 \xrightarrow{\Delta G_{\mathrm{PdO}_{\mathrm{bulk}}}^{\mathrm{form}}} \mathrm{PdO}_{\mathrm{bulk}} (3.5)$	-111	-46	-16
$Pd_{bulk} + Z_2H_2 + \frac{1}{2}O_2 \xrightarrow{\Delta G_{Z_2Pd}^{form}} Z_2Pd + H_2O$ (3.6)	+8	-50	-74
$Pd_{bulk} + Z_2H_2 \rightarrow Z_2Pd + H_2O (3.7)$	+119	-4	-58

species in CHA, represented here by Z₂Pd where 'Z' denotes the substitution of framework Si with Al (Figure 3.3).^{77,89,110} The lowest energy Z_2Pd structure has 2Al in a third nearest neighbor (3NN) arrangement (0 kJ mol⁻¹), followed by the 2NN configuration (+65–80 kJ mol⁻¹).^{77,89,110,111} One Al T-site (1Al) can be charge-compensated by Pd⁺ cations (ZPd), or by Pd²⁺ as [PdOH]⁺ (ZPdOH). The ZPd structure is +28– 60 kJ mol⁻¹ higher in energy than 3NN Z₂Pd.^{77,89} The existence of Pd⁺ after high temperature treatments in air with and without H_2O is debated in literature;⁷⁷ direct characterization of Pd⁺ has been reported only from EPR measurements of Pd/Y zeolites performed under vacuum and after H_2 treatment at 298 K.¹¹² ZPdOH has been identified in detectable amounts only for CHA materials containing a larger number of ion-exchanged Pd²⁺ species than the number of 2Al sites in the 6-MR,⁸⁴ and is computed to be +60-79 kJ mol⁻¹ higher in energy than 3NN Z₂Pd.^{77,89,111} The Pd content of the Pd-CHA-X-ND samples here (Pd/Al = 0.05-0.08) are much lower than the number of available 2Al 6-MR sites quantified by Co^{2+} titration (Co^{2+}/Al = 0.12). Thus, we expect Pd²⁺ in the 6MR 3NN configuration to be the predominant cationic species in our materials; however, for comparison, we also considered 2NN Z_2Pd , ZPd and ZPdOH in the analyses below.
We next computed the thermodynamics of oxidation of bulk metallic Pd (Pd_{bulk}) with O_2 to form either bulk PdO (PdO_{bulk}) or ion-exchanged Pd cations (additional details in Section S5, SI). Table 3.2 reports reaction energies (ΔE) and free energies (ΔG^{form}) for the formation of PdO_{bulk} from Pd_{bulk} (Eq. 3.5), and for the formation of 3NN Z_2Pd sites from either Pd_{bulk} (Eq. 3.6) or PdO_{bulk} (Eq. 3.7), at conditions representative of the high-temperature air treatments (598–873 K, 20 kPa O_2 , impurity H₂O estimated as 0.014 kPa H₂O) of the Pd-CHA-X-ND samples discussed in Section 3.1.2. The conversion of either Pd_{bulk} or PdO_{bulk} to 3NN Z_2Pd sites is endothermic, but thermodynamically favorable (exergonic) at temperatures >576 K $(0.014 \text{ kPa H}_2\text{O}, \log_{10} (P_{\text{O}_2}/P^\circ) > -9.5 \text{ (Figure S5.2, SI)}$. Reaction energies to form 2NN Z_2Pd , ZPd and ZPdOH sites are >27 kJ mol⁻¹ more endothermic than to form $3NN Z_2Pd$ sites (Table S5.1 and Figure S5.2, SI). These results demonstrate that conversion of bulk metallic Pd to either PdO agglomerates or to 3NN Z₂Pd sites is thermodynamically favorable over the range of high-temperature air treatments studied experimentally and suggest that the relative difference in the free energies of PdO agglomerates and Z_2Pd cations will influence Pd speciation.

To compare our thermodynamic predictions to the experimental Pd redispersion data in **Figure 3.2**, we estimated the thermodynamic limit of conversion of Pd particles to Z_2Pd (X_{Z_2Pd}) for a range of particle sizes ($d_{Pd} = 2-100$ nm) by considering a Boltzmann distribution of the equilibrium population of PdO particles and Z_2Pd cations (Eq. 3.8):⁷

$$X_{\rm Z_2Pd}(P_{\rm O_2}, P_{\rm H_2O}, d_{\rm Pd}, T) = \frac{\left(\frac{N_{\rm 2Al}}{N_{\rm Pd}}\right) \exp\left(\frac{-\Delta G_{\rm Z_2Pd}^{\rm form}(P_{\rm O_2}, P_{\rm H_2O}, T) - \Delta G_{\rm PdO}^{\rm form}(P_{\rm O_2}, d_{\rm Pd}, T)}{k_B T}\right)}{\left(\frac{N_{\rm 2Al}}{N_{\rm Pd}}\right) \exp\left(\frac{-\Delta G_{\rm Z_2Pd}^{\rm form}(P_{\rm O_2}, P_{\rm H_2O}, T) - \Delta G_{\rm PdO}^{\rm form}(P_{\rm O_2}, d_{\rm Pd}, T)}{k_B T}\right) + 1}$$
(3.8)

where N_{2Al}/N_{Pd} is the ratio of the number of 6-MR 2Al sites as quantified by Co²⁺ titration,¹¹³ and the number of Pd quantified by ICP. Analogous results for 2NN Z₂Pd, ZPd and ZPdOH are reported in Figure S5.4, SI. Particle size-dependent free energies of Pd and PdO nanoparticles were determined relative to bulk free energies using the free energy model for nanoparticles adhered to a support developed by Campbell and coworkers^{102–104} using calorimetric measurements:

$$\Delta G(d, P_{O_2}, T) = (3\gamma (P_{O_2}, T) - E_{adh}) \left(1 + \frac{1.5}{d}\right) \left(\frac{2\rho}{d}\right)$$
(3.9)

where γ is the particle surface energy (estimated from DFT), E_{adh} is the adhesion energy of the particle to the support (estimated from literature values and our TEM data), d is the particle diameter, and ρ is the volume normalized per mole of Pd; additional details are reported in Section 3.2.4. Expansion of particle volume due to the oxidation of Pd to PdO was accounted for by including a volume expansion factor of 1.19 (described in Section 3.2.4).

Figure 3.4a shows the results for the compositional parameters (N_{2Al}/N_{Pd} and d_{Pd}) corresponding to the Pd-CHA-X-ND zeolites (Table 3.1) and their respective air treatment conditions (Figure 3.2). Blue and yellow regions of Figure 3.4a denote complete conversion of metallic Pd particles to PdO agglomerates and to Z₂Pd sites, respectively. Figure 3.4a shows that complete conversion of 2 nm (squares), 7 nm (circles), and 14 nm (triangles) Pd particles to Z₂Pd is thermodynamically feasible at all the air treatment conditions in Figure 3.2 (598–873 K, 20 kPa O₂, 0.014 kPa H₂O), and these results are insensitive to perturbations in PdO adhesion energy (contact angle varied from 60° to 120°) and surface free energy (\pm 0.2 J m⁻²) within the particle size-dependent free energy model (Figures S5.5-5.6, SI). The thermodynamic predictions for 2 nm particles are consistent with the experimental results for Pd-



Figure 3.4: Pd particle size-dependent thermodynamic phase diagram for the conversion of Pd particles to Z₂Pd in CHA (Si/Al =12, Pd/Al = 0.06) under (a) 20 kPa O₂, 0.014 kPa H₂O and (b) 20 kPa O₂, 6 kPa H₂O, based on HSE06-D3(BJ)vdw calculated energies. The fraction of Pd particles converted to Z₂Pd for 2 nm (squares), 7 nm (circles), and 14 nm (triangles) Pd particles at the experimental air treatment conditions for Pd-CHA-X-ND samples are labeled. (c) Thermodynamic phase diagram for the conversion of 7 nm Pd particle to ion-exchanged Pd²⁺ cations on CHA (Si/Al =12, Pd/Al = 0.06) as a function of temperature and $P_{\rm H_2O}$. The fraction of Pd particles converted to ion-exchanged Pd²⁺ cations of 2, 0.014 kPa H₂O (red circles), and 20 kPa O₂, 6 kPa H₂O (blue circles) at treatment temperatures of 598–1023 K are labeled.

CHA-2-ND, which contained predominantly ion-exchanged Pd^{2+} after treatment to 673 or 773 K. However, for 7 and 14 nm particles, the computed fractions of Pd particles converted to Z₂Pd sites (~1.00) are significantly higher than the amount of ion-exchanged Pd²⁺ observed experimentally for Pd-CHA-7-ND and Pd-CHA-14-ND (598–773 K). Further, our model predicts complete oxidation of metallic Pd with O₂ to mononuclear Pd²⁺ species (i.e., either agglomerated PdO or Z₂Pd) under these conditions; yet, a residual fraction of metallic Pd persists on both Pd-CHA-7-ND and Pd-CHA-14-ND following air treatments (598 K for Pd-CHA-7-ND and 598–873 K for Pd-CHA-14-ND). Air treatment of Pd-CHA-14-ND at 673 K for 1 h and 5 h formed the same amount of ion-exchanged Pd²⁺ and consumed the same amount of H₂ per Pd (Table S4.1 and Figure S4.3, SI). These results, together with our thermodynamic modeling, suggest that complete conversion of large Pd particles (7–14 nm) to ionexchanged Pd²⁺ is not thermodynamically limited at these conditions (598–873 K, 20 kPa O₂, 0.014 kPa H₂O), and that kinetic barriers are instead responsible for the incomplete oxidation and disintegration of large Pd particles into ion sites.

3.3.1.4 Effect of H_2O on the Conversion of Agglomerated Pd Particles to Exchanged Pd^{2+} Ions.

The addition of H_2O to the air stream has been proposed to facilitate the mobility of Pd, causing a greater fraction of agglomerated PdO domains to convert to Pd^{2+} cations.⁶³ To determine the thermodynamic influence of H_2O pressure on Pd structural interconversion, we constructed phase diagrams for air treatment conditions with higher H_2O partial pressures (6 kPa). **Figure 3.4b** shows the fraction of Pd particles converted to Z_2Pd at the different treatment temperatures studied for Pd-CHA-X-ND samples, which are labeled for comparison with **Figure 3.4a**. We considered a representative Pd particle size of 7 nm and show its conversion to Z_2Pd as a function of temperature and P_{H_2O} in **Figure 3.4c** at treatment conditions of 20 kPa O₂ with 0.014 kPa H₂O (red circles) and 6 kPa H₂O (blue circles). Analogous phase diagrams for Pd particle sizes of 2 and 14 nm are reported in Figure S5.12, SI.

Our results predict that increasing $P_{\rm H_2O}$ thermodynamically limits the amount of Z₂Pd formed, and while the X_{Z_2Pd} values predicted vary within \pm 20% (Figures S5.9–5.11, SI) depending on the precise values used for nanoparticle adhesion and surface energy, they are consistently lower than those predicted in dry air conditions (Figure 3.4a). The inhibiting effect of H_2O is especially pronounced for larger Pd particles at temperatures <773 K. Our model predicts that 7 and 14 nm Pd particles almost fully convert to ion-exchanged Pd^{2+} during air treatments >600 K in the presence of 0.014 kPa H_2O (Figure 3.4a), but that the conversion of Pd particles decreases (to 0.31 and 0.19 for 7 and 14 nm, respectively) when $P_{\rm H_2O}$ is increased to 6 kPa (**Figure 3.4b**). Conversely, the effect of higher $P_{\rm H_2O}$ at temperatures >600 K is negligible for 2 nm Pd particles, which are predicted to fully convert to Z_2Pd during air treatments in the presence of 0.014 or 6 kPa H₂O. At conditions typically representative of practical PNA applications $(2.5-6 \text{ kPa H}_2\text{O})$,⁴⁸ an increase in $P_{\rm H_2O}$ favors formation of larger fractions of PdO agglomerates at temperatures ${<}800$ K for $d_{\rm Pd}$ = 2–14 nm. The H_2O promoted formation of agglomerated PdO becomes attenuated with increasing temperature due to the increase in the entropic contribution of H_2O formation relative to the enthalpy of reaction (Figure S5.13, SI). Consequently, complete conversion of Pd particles to Z_2Pd is again predicted for all the Pd-CHA-X-ND zeolites at temperatures >800 K.

Our thermodynamic predictions suggest that adding H_2O to air streams would inhibit the structural transformation of agglomerated PdO domains to ion-exchanged



Figure 3.5: (a) The amount of ion-exchanged Pd^{2+} and (b) total H₂ consumed normalized per total Pd as a function of treatment temperature in flowing air (squares), 6 kPa H₂O in balance air (circles), air (1 h) then adding 6 kPa H₂O (1 h, diamond), and 6 kPa H₂O in balance air (1 h) then air (1 h, triangle) for the Pd-CHA-7-ND material. Dashed line represents theoretical maximum values. H₂ TPR profiles are reported in Figure S4.7, SI.

Pd²⁺ cations. To experimentally test these predictions, the as-deposited Pd-CHA-7-ND sample was treated in either flowing air with 6 kPa H_2O or without H_2O at temperatures between 673–973 K, and the ion-exchanged Pd^{2+} content and H_2 consumption (per Pd) were quantified with H₂ TPR. Figure 3.5 and Table S4.3, SI show that fewer ion-exchanged Pd²⁺ sites were formed and the PdO content increased after the wet air treatment in comparison to the dry air treatment at temperatures <900 K, which is qualitatively consistent with our thermodynamic predictions (Figure 3.4) that increasing H_2O pressures should reduce Pd^{2+} cation content and increase the agglomerated PdO content. Similar results have been reported for atomically dispersed Pt on CeO_2^{114} where steam exposure led to an increase in particle agglomeration. Additionally, a larger fraction of residual metallic Pd remained after wet air treatments than after dry air treatments for temperatures between 673 and 873 K, an effect that may be due to H_2O -induced hydroxylation of particle surfaces inhibiting the complete oxidation of Pd.¹¹⁵ Treatment of Pd-CHA-7-ND in air at 973 K with and without H_2O resulted in the same amount of ion-exchanged Pd^{2+} (0.80–0.85 per total Pd) and H_2 consumption (0.87-0.88 per total Pd), consistent with the absence of an H₂O pressure dependence on our thermodynamic predictions at 973 K (Figure 3.4). Analogous experiments on Pd-CHA-2-ND (Figures S4.4-4.5, SI) evidence no residual metallic Pd, and similar fractions of Pd^{2+} and PdO when either air alone or air and 6 kPa H_2O were co-fed, consistent with thermodynamic predictions that the effect of H_2O becomes attenuated for small particle sizes (Figure 3.4b). Together, our thermodynamic and experimental results demonstrate that co-feeding H₂O at temperatures of 673-873 K does not facilitate the transformation of PdO to ion-exchanged Pd^{2+} , in contrast to proposals in previous studies⁶³ wherein the treatment temperature itself was likely the dominant influence on the extent of agglomerated PdO converted to ion-exchanged Pd²⁺ cations. Instead, water promotes the formation of PdO, and this

effect becomes attenuated with decreasing particle size and increasing temperature.

The decrease in cation formation when H_2O is co-fed (673–873 K) could reflect consequences of H_2O inhibiting the kinetics of Pd redispersion to Pd^{2+} cations, or changing the thermodynamic equilibrium to promote the formation of PdO agglomerates from Pd^{2+} cations, in the latter case as suggested by our thermodynamic calculations and formation of H_2O as a product in the cation exchange reaction (Eq. 3.7). To determine if Pd^{2+} cations could reversibly transform to PdO agglomerates under wet conditions, the as-deposited Pd-CHA-7-ND sample was first treated in flowing dry air to 673 K and held for 1 h, and then exposed to a wet air stream (6 kPa H_2O stream for 1 h (Figure 3.5, green diamond). The amount of ion-exchanged Pd^{2+} (per total Pd) decreased from 0.72 (dry air) to 0.59 (dry air followed by wet air), but did not reach the value measured on the sample exposed only to the wet air treatment (0.43). These results demonstrate that starting from a distribution of Pd^{2+} cations and PdO agglomerates the addition of H_2O to the air stream results in the loss of Pd^{2+} cations, an effect that shows that the reaction $Z_2H_2 + PdO \Leftrightarrow$ $Z_2Pd + H_2O$ becomes reversible at 6 kPa H_2O , an effect that must be driven by thermodynamics.

To further confirm that PdO agglomerates form from Pd^{2+} cations under hydrous conditions, and the generality of this observation, analogous experiments were performed at 673 K and 773 K on the Pd-CHA-2-ND sample. The sample was treated in flowing dry air to 673 K and held for 1 h, and then exposed to a wet air stream (6 kPa H₂O) stream for 24 h, and the Pd speciation quantified using H₂ TPR (Figure S4.5 and **Table 3.3**). Exposure to the wet air stream decreased the fraction of ion-exchanged Pd²⁺ (per total Pd) from 0.83 (dry air) to 0.71 (dry air followed by wet air), and resulted in a concomitant increase of PdO from 0.17 (dry air) to 0.27 (dry

	673 K			$773~{ m K}$
	$673~{ m K}$	subsequent	$773~{ m K}$	subsequent
	air	air/ water	air	air/ water
PdO agglomerates/ Pd_{tot}	0.17	0.27	0.00	0.02
Mononuclear $\mathrm{Pd}^{2+}/$ $\mathrm{Pd}_{\mathrm{tot}}$	0.83	0.71	1.08	1.00
H_2 consumed/ Pd_{tot}	1.00	0.98	1.08	1.02

Table 3.3: Pd Speciation After 673 K and 773 K Sequential Air and Air/Water Treatments on Pd-CHA-2-ND^a

^a H₂ TPR profiles reported in Figure S4.14, Supporting Information.

air followed by wet air). Similar experiments performed at 773 K (Figure S4.14, Table S4.5, SI) showed an increase from 0.00 to 0.02 of the fraction of PdO after air/water exposure, consistent with the suppression of PdO formation at small particle sizes and higher temperatures predicted in **Figure 3.4b**.

Introducing H₂O to the 673 K air stream after 1 h treatment of Pd-CHA-7-ND did not reversibly generate the same distribution formed after the H₂O-only treatment; moreover, a longer treatment time (18 h) in the wet air stream following an air-only treatment did not change the ion-exchanged Pd²⁺ content or H₂ consumption per total Pd (Table S4.2 and Figure S4.6, SI), demonstrating that the values reported after a 1 h treatment in **Figure 3.5** reflect a pseudo steady-state distribution of agglomerated PdO and ion-exchanged Pd²⁺. Additionally, the reverse experiment was performed where the Pd-CHA-7-ND sample was first treated in wet air (6 kPa H₂O) to 673 K for 1 h, followed by removing the H₂O from the air stream and holding for 1 h. The resulting ion-exchanged Pd²⁺ (per total Pd) increased slightly from 0.43 (wetted air only) to 0.49, which was significantly below the result on the sample exposed only to a dry air treatment (0.72). The partially irreversible nature of Pd structural interconversion between dry and wet (6 kPa H₂O) air treatments can be rationalized from conclusions of prior work⁸⁴ that showed sample treatment history influences the spatial distribution and particle sizes of Pd domains. Here, the first dry air treatment (673 K, 1 h) of Pd-CHA-7-ND converted the 7 nm Pd particles initially present at the exterior zeolite crystallite to different PdO domain sizes and ion-exchanged Pd²⁺ sites distributed deeper within the interior of zeolite crystallites; thus, upon subsequent addition of H₂O to the flowing air stream, there was a different distribution of PdO particle sizes with some amount of ion-exchange Pd²⁺. Consistent with these observations, exposure of the Pd-CHA-2-ND sample to air at 1023 K, followed by air/water at 773 K did not result in formation of PdO (Figure S4.14, SI). Taken together, our results show that at low temperatures the addition of H₂O to flowing air generates a thermodynamic driving force for the reverse exchange reaction to occur (Eq. 3.7), forming PdO agglomerates from Pd²⁺ cations, and that the sample history and spatial distribution of Pd²⁺ sites are important factors in the extent of reversibility between Pd²⁺/PdO distributions.

3.3.2 Quantifying Apparent Rates of Pd Redispersion

3.3.2.1 Effect of Treatment Temperature and H_2O on Rates of Pd Redispersion.

To deduce mechanistic information for structural interconversion, we monitored the conversion of agglomerated, metallic Pd domains to ion-exchanged Pd²⁺ sites as a function of time under flowing air at different temperatures. To explore the effects of the functional form of the particle size distribution on redispersion rates, a suite of Pd-CHA-X-LND samples were synthesized to contain varying average particle sizes



Figure 3.6: (a) The amount of ion-exchanged Pd^{2+} normalized per total Pd as a function of time during isothermal switching experiments for three different treatment temperatures (square: 673 K, triangle: 648 K, circle: 598 K) using the Pd-CHA-2.9-LND sample, (b) The total H₂ consumed normalized per total Pd from (a). Dashed line represents theoretical maximum amount. H₂ TPR profiles are in Figures S4.9 S4.11, SI.

(X=2.1, and 2.9 nm), using synthesis approaches that led to a more log-normally distributed particle size distribution (denoted by 'LND' in the sample nomenclature, synthesis and characterization details in Section S1, SI) than samples prepared by colloidal Pd nanoparticle synthesis approaches.⁸⁵

Figure 3.6 shows the amount of ion-exchanged Pd^{2+} as a function of time and temperature for the isothermal Pd redispersion rate measurements (further discussion on rate measurements in Section S6, SI) of the Pd-CHA-2.9-LND sample. The amount of ion-exchanged Pd^{2+} formed after treatment in air for 1 h increased systematically with temperature, which agrees with thermodynamic predictions (Section 3.3.1.3) that higher temperatures facilitate the conversion of agglomerated PdO parti-



Figure 3.7: (a) The amount of ion-exchanged Pd^{2+} (normalized per ion-exchanged Pd^{2+} content after treatment for 1 h, and denoted as conversion) as a function of time during isothermal switching experiments performed at 648 K for Pd-CHA-2.9-LND sample in air (circles), 2 kPa H₂O in balance air (squares), and Pd-CHA-2.1-LND in air (diamonds). H₂ TPR profiles are in Figures S4.10, S4.12, and S4.13, SI. (b) H₂ consumed normalized to total Pd of materials in (a).

cles to ion-exchanged Pd^{2+} , and is consistent with an activated process for structural interconversion. **Figure 3.6b** shows that the H₂ consumption per Pd was approximately unity for all time points after 10 s, suggesting the observed ion-exchanged Pd^{2+} formation rates were not limited by metallic Pd oxidation to PdO with O₂. This observation demonstrates the mechanistic role of O₂ is only to oxidize metallic Pd; thus, the reported formation of ion-exchanged Pd^{2+} as a function of time reflects the rate of structural conversion of agglomerated PdO domains to ion-exchanged sites.

To determine the kinetic influence of H_2O on the apparent redispersion rate, we performed isothermal redispersion experiments on the Pd-CHA-2.9-LND sample with and without 2 kPa H_2O (**Figure 3.7**). Consistent with previous thermodynamic arguments, adding 2 kPa H_2O to the inlet air stream decreased the amount of ion-exchanged Pd^{2+} cations after treatment for 1 h (Figure S6.1, SI); however, when the amount of exchange was normalized to the pseudo steady state value after 1 h (i.e., normalizing rates to the reversible fraction of Pd that can interconvert), the apparent rates of redispersion with and without H₂O were similar within error. Additionally, the H₂ consumption per total Pd was approximately unity for all time points measured, again demonstrating the rate of Pd redispersion was not limited by Pd oxidation. Therefore, co-feeding H₂O did not have a significant kinetic effect on the redispersion of PdO particles to ion-exchanged Pd²⁺ and, for this material and conditions of these measurements, H₂O apparently only influences the thermodynamics of the redispersion process.

Time-dependent redispersion measurements of the Pd-CHA-2.1-LND sample (**Figure 3.7**) showed faster apparent rates of redispersion to ion-exchanged Pd^{2+} . Notably, the shortest time point of 10 s resulted in almost complete conversion (0.9) of the Pd species that reversibly convert between agglomerated domains and ion-exchanged Pd^{2+} . Additionally, all the redispersion rates measured for Pd-CHA-2.1-LND showed H₂ consumptions per Pd near unity. These data suggest smaller Pd nanoparticles disintegrate at a faster rate for structural interconversion to ion-exchanged Pd^{2+} .

3.3.2.2 Kinetic Models for Pd Redispersion

Experimental data and atomistic simulation results for supported metal particles suggest that Ostwald ripening (OR) is the predominant mechanism for the disappearance of small nanoparticles and sintering compared to particle migration and coalescence.^{22,116} The OR process is associated with the rapid disappearance of particles smaller than a critical radius, generating a pool of monomers that transport be-





tween particles through either gas phase or surface diffusion processes, resulting in the formation of larger particles. In contrast to conventional OR mechanisms, in the presence of framework Al ion-exchange sites in the zeolite support, we hypothesize that monomers ejected from the surface of PdO particles form either larger PdO agglomerates or ion-exchanged Pd^{2+} via an atom trapping mechanism (Scheme 3.1). Figures 3.6 and 3.7 demonstrate that oxidation of metallic Pd to PdO is rapid relative to the rate of redispersion to Pd^{2+} cations, therefore we consider PdO to be the initial state of the particles in the redispersion mechanism. Plausible monomer-facilitated mechanisms proposed for the conversion of PdO nanoparticles to ion-exchanged Pd^{2+} involve the detachment of neutral, mobile species, such as Pd_1O_1 and $Pd_1(OH)_2$ from PdO agglomerates, and their successive reactions with the zeolitic Brønsted acid sites.^{7,84,117} There are established kinetic models for OR-based particle sintering for

supported metal catalysts,^{27,118,119} however, kinetic models have not been reported that incorporate monomer migration and subsequent atom trapping of monomers on surface/lattice defect or cation exchange sites.

Ripening of nanoparticles occurs by diffusion of monomers through the gas phase or on a substrate.^{27,120–126} Wynblatt and Gjostein proposed that monomer transport via the gas phase takes place for metals with volatile metal oxides such as Pt.¹¹⁸ Simulation results reported by Plessow et al. for dispersed Pt particles on silica using a modified Wynblatt-Gjostein gas-phase sintering model show agreement with the experimental data in the high-temperature regime (>1023 K) where higher oxygen pressures accelerated sintering via formation of volatile $Pt_1O_2(g)$.¹²⁷ Recently, Goodman et al. performed similar gas-phase sintering simulations for Pd/SiO₂ to demonstrate that emission of Pd atoms in the vapor phase becomes substantially higher (5 atoms s⁻¹ from a 8.8 nm Pd particle) with an increase in Pd vapor pressure at temperatures >1173 K.¹²⁸ Although the air treatment temperatures reported here (598–1023 K) are lower than those where gas-phase sintering has been shown to become appreciable, we explored the possibility of both gas-phase and substrate-mediated Pd redispersion.

To determine the feasibility of a gas phase OR process, we next computed the rate of formation of the most stable gas-phase Pd monomer, which was found to be $Pd(OH)_2(g)$ (details in Section S8.1.1, SI), consistent with prior reports.⁷ We estimated the pressure (P_k) of ejected $Pd(OH)_2$ (g) monomers in equilibrium with a PdO nanoparticle comprised of k atoms as:⁷

$$PdO_{bulk} + H_2O \xrightarrow{\Delta G_{Pd(OH)_2(g)}^{form}} Pd(OH)_2(g)$$
 (3.10)

$$P_k = P_{\rm H_2O} \, \exp\left(\frac{-\Delta G_{\rm Pd(OH)_2(g)}^{\rm form} + \frac{A_k\gamma}{k}}{k_B T}\right) \tag{3.11}$$

where γ is the average surface energy of the PdO surface from which monomers detach, A_k is the surface area of the particle, and $\Delta G_{Pd(OH)_2(g)}^{form}$ denotes the formation free energy of Pd(OH)₂(g) relative to bulk PdO. For a system with a distribution of particle sizes, the background pressure (P_b) of Pd(OH)₂(g) is given by:¹²²

$$P_{\rm b} = \frac{\sum_k A_k n_k P_k}{\sum_k A_k n_k} \tag{3.12}$$

where n_k is the surface density of the nanoparticle, and P_k is the equilibrium pressure of monomers calculated using Eq. 3.11. Subsequently, the influx of Pd(OH)₂(g) monomers J_k (monomers nm⁻² s⁻¹) received by a PdO nanoparticle comprised of katoms can be estimated using kinetic theory of gases:

$$J_{k} = \frac{(P_{\rm b} - P_{\rm k})}{\sqrt{2\pi m_{\rm Pd(OH)_{2}(g)}k_{\rm B}T}}$$
(3.13)

where $m_{\rm Pd(OH)_2(g)}$ is the molecular mass of Pd(OH)₂(g). A lower background monomer pressure would correspondingly result in a lower monomer flux. For example, at 6 kPa H₂O, 20 kPa O₂, and 873 K, the particle size distribution for the Pd-CHA-7-ND sample (Figure S2.8, SI) generates a background monomer pressure of only 3.2×10^{-16} kPa, and 3.6×10^{-7} Pd(OH)₂ (g) monomers per second colliding with the surface of a 7 nm particle in the distribution. In comparison, a similar Pt particle size distribution has a collision frequency of 25 PtO₂ (g) monomers s⁻¹ because of its substantially higher background monomer pressure (2.8×10^{-8} kPa). We also considered other plausible scenarios (e.g. PdO(g)) for gas phase monomer formation (Table S8.2, SI), but all such routes have fluxes that are even lower than the formation of $Pd(OH)_2(g)$ from PdO agglomerates. The maximum rates of ionexchange (Section S8.1.3, SI) for the Pd-CHA-7-ND and Pd-CHA-2.9-LND samples (**Figure 3.7**) are 10^{-15} s⁻¹ (673 K, $d_{avg} = 7$ nm), and 10^{-13} s⁻¹ (648 K, $d_{avg} = 2.9$ nm), respectively. The observed rate of ion-exchange for Pd-CHA-2.9-LND (~ 10^{-4} s⁻¹) and the time scale reported in our experiments (**Figure 3.2**) for complete ion-exchange of Pd-CHA-7-ND (~1 h) are orders of magnitude faster than the computed gas phase rates.

The available data show that Pd redispersion does not occur through the gas phase at temperatures <900 K. First, the observed redispersion rates at the conditions of our experiments are at least ~9 orders of magnitude faster than what would be expected for a gas phase process. Challa et al.¹²³ invoked similar calculations for emission of Ni monomers to show that monomers transport on the support during the disappearance of small Ni nanoparticles supported on MgAl₂O₃. Second, since Pd(OH)₂(g) monomer flux is directly proportional to $P_{\rm H_2O}$ in a gas phase process (Eq.s 3.10 and 3.11) changes in $P_{\rm H_2O}$ should reflect changes on the rates of formation of ion-exchanged Pd²⁺.

For example, comparison of experimental and simulation results for isothermal Pt sintering (873 K) showed faster rates of sintering with increases in P_{O_2} .¹²⁷ However, as evidenced by the results of the isothermal redispersion air treatment with and without 2 kPa H₂O (**Figure 3.7**), there was no change in the apparent rates of redispersion, again suggesting that diffusion of monomers on the zeolite substrate is the dominant process. Finally, if the OR process occurred via gaseous monomers, it would be expected that all oxidized Pd would disintegrate and form cations, but this is not the case as demonstrated in **Figure 3.2**. Taken together, these results imply

that interconversion of Pd particles to ion-exchanged Pd occurs through diffusion of monomer species on the zeolite substrate at temperatures <900 K.

To elucidate the particle size dependent nature of the redispersion of PdO agglomerates and ion exchange process, we next incorporated an atom trapping surface reaction assumed to be first order in both Z_2H_2 exchange sites and mean-field substrate monomer concentration:

$$\frac{\mathrm{dZ}_{2}\mathrm{H}_{2}}{\mathrm{d}t} = -k_{\mathrm{rxn}}[\mathrm{Z}_{2}\mathrm{H}_{2}] \,[\mathrm{monomer}]$$
(3.14)

into the system of differential equations that correspond to the mass balance of a substrate-mediated OR kinetic model^{121–123} that accounts for activated monomer formation, activated diffusion of monomers on a substrate, and exchange of monomers between particles comprised of k Pd atoms:

$$\frac{\mathrm{d}C_k}{\mathrm{d}t} = -K_{\mathrm{os}}C_{\mathrm{inf}} \left| \exp\left(\frac{G_{k*}}{k_B T}\right) - \exp\left(\frac{G_k}{k_B T}\right) \right| C_k d_k + (\mathrm{generation}) \tag{3.15}$$

where, C_k is the particle number density (particles nm⁻²), ΔG_k is the nanoparticle free energy with respect to bulk PdO (computed using the relation developed by Campbell et al. in Eq. 3.9), K_{os} is the lumped pre-exponential factor for OR, C_{inf} is the far-field concentration of monomers in equilibrium with an infinite size particle at an infinite distance from the particle-support interface, and d_k is the effective particle diameter (Table S8.1, SI). Full details of the OR kinetic model are reported in Section S8.2, SI. Depending on the number of Pd atoms that correspond to the critical particle radius (k_* , determined at each time step as described in Section S8.2, SI), a particle will either grow $(k > k_*)$ by consuming monomers or shrink $(k < k_*)$ by detaching monomers. The generation term represents formation of a new particle with k Pd atoms:

$$(\text{generation}) = \begin{cases} K_{\text{os}}C_{\text{inf}} \left| \exp\left(\frac{G_{k*}}{k_BT}\right) - \exp\left(\frac{G_{k-1}}{k_BT}\right) \right| C_{k-1}d_{k-1} \text{ if } k > k_* \\ 0 & \text{if } k = k_* \\ K_{\text{os}}C_{\text{inf}} \left| \exp\left(\frac{G_{k*}}{k_BT}\right) - \exp\left(\frac{G_{k+1}}{k_BT}\right) \right| C_{k+1}d_{k+1} \text{ if } k < k_* \end{cases}$$
(3.16)

Eq. 3.15 shows that the driving force for the OR process, $\left| \exp\left(\frac{\Delta G_{k*}}{k_B T}\right) - \exp\left(\frac{\Delta G_k}{k_B T}\right) \right|$, originates from the free energy difference between nanoparticles of different sizes. The resulting monomer mass balance is:

$$\frac{\mathrm{d}[\mathrm{monomer}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Z}_{2}\mathrm{H}_{2}]}{\mathrm{d}t} + \sum_{k=2}^{k_{*}} \frac{\mathrm{d}C_{k}}{\mathrm{d}t} - \sum_{k=k_{*}}^{\max k} \frac{\mathrm{d}C_{k}}{\mathrm{d}t}$$
(3.17)

and describes monomer consumption due to atom trapping at Z_2H_2 sites, generation of monomers from smaller particles, and consumption of monomers by larger particles.

The four model parameters are the rate constant for cation exchange from monomers (k_{rxn} , nm² s⁻¹), the OR rate constant associated with activated diffusion of monomers (K_{os} , nm s⁻¹), the far-field concentration of monomers (C_{inf} , nm² related to the monomer formation energy), and the surface energy of the nanoparticles (γ , J m⁻² implicit in ΔG_k). Typical reported values for these parameters are shown in Table S8.5, SI. We randomly generated initial Pd particle size distributions that are consistent with the log-normal distribution (LND) means and standard deviations of the experimentally observed particle size distributions for the Pd-zeolite samples in **Figure 3.7** (Table S2.1, SI). We started by assuming these particles oxidize rapidly and their initial state is PdO, as evidenced by **Figures 3.6b** and **3.7b**, and then used kinetic Monte Carlo (kMC) to solve the resulting system of differential equations (Section S8.2, SI) for the particle size distribution, monomer concentration, and the fraction of ion exchange as a function of time. The randomly generated particle size distributions, and kMC itself, give stochastic results; therefore, the results from 350 independent kMC simulations were averaged to generate predictions for the fractional extent of ion exchange. Figure S8.3, SI shows that by 250 kMC simulations results are converged. We regressed the four model parameters using only the measured conversion of Pd-CHA-2.9-LND (**Figure 3.7**); regressed OR parameter values fall into the ranges of those previously reported (Table S8.5, SI) and the regressed surface energy is within 0.1 J m⁻² of our DFT-computed value.

Figure 3.8 reports kMC results starting from a log-normal distribution (LND) of nanoparticles, consistent with the samples prepared via incipient wetness impregnation (Pd-CHA-2.1-LND (red traces), Pd-CHA-2.9-LND (green traces)), or a normal distribution (ND), consistent with the samples prepared from monodisperse Pd particles via colloidal synthesis (Pd-CHA-2-ND (blue traces, 2.2 nm, particle size distribution in Figure S2.7, SI), Pd-CHA-7-ND (purple traces, 6.9 nm, particle size distribution in Figure S2.8, SI)). The model predicts that larger particles (2.9 nm) have slower rates of ion-exchange compared to the smaller particles (2.1 nm) and captures the differences in rate between the two particle size distributions that are observed experimentally (**Figure 3.7**). We emphasize that the regressed model parameters are not particle size-dependent, and the effect of particle size on kinetics is described solely by the physics of OR and atom trapping in the model. Smaller par-



Figure 3.8: (a) The kMC predicted redispersion kinetics at T = 648 K. Model parameters were estimated by fitting the 2.9 nm averaged log-normally distributed (LND) sample (red traces) to experimentally measured conversion (red circles). The error bars denote one standard deviation of experimental measurements. (b) Initial simulated Pd particle size distributions. (c) The evolution of PdO particle size distributions as a function of time, the number on the top right in each histogram shows the conversion of Pd atoms in PdO particles to exchanged Pd²⁺. Simulation results for t < 1 s are shown in Figure S8.4, SI.

ticles result in a higher substrate monomer concentration, which drives the exchange reaction, and has a strong dependence on particle size. As released monomers are consumed by the faster trapping reaction the particles continue to lose monomers onto the substrate, and the exchangeable fraction of Pd for all distributions is completely exhausted within 1000 s. Figure 3.8b shows that the narrower particle size distributions for the ND samples (Pd-CHA-2-ND) result in faster rates of ion exchange compared to the LND samples with similar average particle size (Pd-CHA-2.1-LND and Pd-CHA-2.9-LND), because the largest particles located in the trailing tail of the LND particle size distribution are the slowest to disintegrate. The Pd-CHA-7-ND sample is predicted to reach complete conversion of exchangeable Pd by 400 s, which is consistent with experimental observations that full ion-exchange is reached within 1 h. The model predicts the Pd-CHA-7-ND sample will reach complete conversion more rapidly than the Pd-CHA-2.9-LND, highlighting the effect of size distribution. The Pd-CHA-7-ND sample has a longer induction period than Pd-CHA-2.9-LND (Figure S8.4, SI), however, once redispersion starts, the majority of particles in a tighter distribution will quickly release monomers. Although the unexchangeable fraction of Pd reported in **Figure 3.2** is not accounted for in our kinetic model, the substratemediated OR model accurately describes the kinetics of the exchangeable Pd fraction, suggesting that the experimentally observed incomplete ion-exchange likely reflects the non-mean-field nature of diffusion through a porous three-dimensional substrate and the spatial arrangement of particles at external zeolite crystallite surfaces. The K_{os} and k_{rxn} parameters depend on interparticle distances, and distances between particles and exchange sites, respectively, and their regressed values represent a weighted average over different local environments of particles in the samples. These parameters may vary with changes in the spatial distribution of particles^{7,129} and exchange sites, and do not account for pore blocking, which may result in incomplete ionexchange.^{130,131} Further, the molecular structure(s) of the monomer intermediates formed on the zeolite substrate are unknown; their energetics in our model are described by the regressed k_{rxn} , K_{os} , and C_{inf} parameters. Nevertheless, our kinetic model captures the observed kinetic dependence of redispersion on particle size and demonstrates that integration of atom trapping kinetics with an OR kinetic model is consistent with the available experimental data.

3.4 Conclusions

We combined precise catalyst synthesis techniques, quantitative site characterization methods, and computational thermodynamic and kinetic models to examine the relative importance of the thermodynamic and kinetic factors governing the interconversion of Pd nanoparticles and ion-exchanged Pd²⁺ cation sites in CHA zeolites under high temperature (593–973 K) air treatments with and without H_2O . To facilitate quantitative measurements of Pd particle redispersion rates and their dependence on the Pd initial particle size and particle size distribution, we prepared a series of Pd-CHA materials using two different synthetic approaches; deposition of colloidal Pd nanoparticle suspensions to form monodisperse, normally distributed Pd particles of different sizes (2–14 nm), and incipient wetness impregnation yielding log-normally distributed particles of varying average sizes (2.1 and 2.9 nm). Smaller Pd nanoparticles (2 nm) readily converted to ion-exchanged Pd^{2+} species in air. The conversion of larger metallic Pd nanoparticles (7, 14 nm) to PdO domains and ion-exchanged Pd²⁺ was observed to be lower than the thermodynamic distributions predicted by DFT, indicating that larger metallic particles have kinetic barriers for oxidation with O_2 to PdO and for the subsequent disintegration of PdO to ion-exchanged Pd^{2+} sites. Additionally, increasing the H_2O partial pressure shifts the thermodynamic distribution away from Pd^{2+} sites and toward agglomerated PdO domains, suggesting that H_2O present in exhaust streams facilitates Pd deactivation to PdO agglomerated phases. Our results suggest that the widely observed agglomeration and deactivation of Pd cation-exchanged zeolites in low temperature hydrous environments (e.g. Wacker oxidation, automotive exhaust, and PNAs) reflect thermodynamic factors that may be deleterious to the long-term storage and stability of atomically-dispersed Pd-zeolite materials.

To deduce mechanistic information of the Pd redispersion process, quantitative measurements of Pd nanoparticle conversion to ion-exchanged Pd^{2+} sites in air with and without H_2O were performed isothermally (598–673 K) with varying treatment time (0.003-1.0 h). The oxidation of metallic Pd with O₂ is complete after 0.003 h of treatment time, and thus kinetically irrelevant for apparent rates of PdO conversion to ion-exchanged Pd²⁺ sites. Additionally, a predominantly PdO-containing CHA material treated in either inert (He) or air to 648 K resulted in similar extents of PdO conversion to ion-exchanged Pd²⁺, further reinforcing that the dominant mechanistic role of O_2 is to oxidize agglomerated metallic Pd to PdO. In the presence of H_2O , the extent of interconversion from Pd^{2+} to PdO is lower when following higher temperature pretreatments, suggesting that Pd^{2+} ions located deeper in the zeolite crystallite are kinetically inaccessible at these conditions.⁸⁴ Under these conditions, quantum chemical calculations predict $Pd(OH)_2(g)$ is the most thermodynamically favorable gaseous Pd species, suggesting that adding H_2O to the air stream may facilitate hydroxylation of the PdO surface to increase the rate of forming $Pd(OH)_2(g)$ intermediates. However, computed rates of gas-phase redispersion kinetics are orders of magnitude slower than experimentally observed rates, and experiments performed

with H_2O (2 kPa) added to the air stream (648 K) show that H_2O pressure (0–2 kPa) did not influence Pd redispersion rates normalized by the fraction of Pd that reversibly interconverts between particles and cation sites. These observations show that H_2O strongly influences the thermodynamics, but not the kinetics, of Pd structural interconversion at 648 K. Smaller Pd nanoparticles result in faster disintegration rates and a greater thermodynamic driving force to form ion-exchanged Pd²⁺. Our kMC simulations of a surface-diffusion mediated OR process, with exchange of mobile Pd species at ion-trapping sites in the zeolite support (formed by Al substitution), are consistent with the particle size dependent kinetics observed experimentally and capture the observed trends with respect to particle size and distribution. Monodisperse particles exhibited faster rates of redispersion compared to log-normally distributed Pd particles because the largest particles in the tail of the distribution require the longest time to disintegrate to monomers.

We conclude that gas phase conditions, initial Pd nanoparticle sizes, and particle size distributions (ND vs. LND), influence the critical thermodynamic and kinetic factors that govern Pd redispersion to ion-exchanged Pd^{2+} sites, which are the desired precursor Pd structures for PNA, Wacker oxidation, and other applications. More broadly, we show that low-temperature (<900 K) Pd redispersion does not occur through gas-phase intermediates, but rather a surface-mediated OR process in the presence of atom trapping sites, as recently suggested by Datye and coworkers for noble metals on ceria supports.² Our results suggest that at low temperatures (<900 K), similar processes may govern the redispersion of Pd nanoparticles on other oxide supports; thus, the non-mean field nature of diffusion on the support and the spatial distribution of particles and atom or ion trapping sites are important factors to consider in strategies to enhance or suppress the rate of redispersion of Pd and PdO particles into site-isolated cations.

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Chapter 4

Thermodynamics and kinetics of interconversion between platinum nanoparticles and cations in zeolites.

I am a co-first author of the work described in this chapter studying thermodynamics and kinetics of Pt particle redispersion in zeolites. The manuscript of this work (Jayaraman, A.; Wijerathne, A.; Mandal, K.; Gounder, R., and Paolucci, C. Thermodynamics and kinetics of interconversion between platinum nanoparticles and cations in zeolites. *J. Catalysis, Under review*) is currently under review, and we are addressing minor revisions. My contribution to this work is (1) Setting up the code for kinetic simulations of the system, (2) Do DFT calculations for estimating the adhesion energy between SiO₂ and Pt, and (3) writing the kinetics section and revising the manuscript.

4.1 Introduction

The catalytic behavior of supported Pt catalysts is affected by particle sintering and redispersion,¹⁻⁶ which are processes that dynamically restructure Pt sites and their ensembles in ways that may activate or deactivate specific active sites. The optimal active site structure depends on the catalyst application and may consist of a single or multiple metal atoms, 3,6-8 and depending on the reaction environment these species can dynamically interconvert between single atoms and nanoparticles via particle redispersion and agglomeration processes.^{1,2,9,10} Redispersion and sintering are also affected by the nature of the support,^{11–14} which further alters Pt site interconversion thermodynamics and kinetics. Therefore, an improved fundamental understanding of the thermodynamic and kinetic factors that influence redispersion and agglomeration processes for supported Pt particles would provide more precise guidance for identifying synthesis and regeneration conditions for Pt catalysts on different support materials. Here, we develop and demonstrate computational approaches for modeling the thermodynamics and kinetics of interconversion between cations and nanoparticles for Pt-containing aluminosilicate zeolites and contribute to the emergent topic of modeling catalyst stability and regeneration.

Zeolites have been widely investigated as potential supports to attenuate the sintering of metal nanoparticle catalysts by providing binding sites and void spaces that can stabilize small metal clusters and single atoms. For Pt supported on zeolites, the stabilization of single Pt atoms at anchoring sites^{1,2,4,9,10,15} is facilitated by the altered electronic structure and coordination of the metal to siloxane or aluminosiloxane rings within the zeolite framework.^{1,16} The three-dimensional, cage-like structure of zeolites confers additional sintering resistance due to high energy barriers (≈ 1.12 -2.57 eV) associated with metal atom diffusion through zeolite pores.^{4,16} Nevertheless, under certain reaction conditions, Pt particles or the atoms that comprise them may mobilize, enabling interconversion between different Pt metal structures.^{1,2,4,9} The thermodynamics and kinetics of particle restructuring depend on the zeolite composition and topology, environmental conditions, and particle size. Under high temperature oxidative conditions, particles may disintegrate into smaller particles or single atoms. Conversely, low temperature reducing conditions facilitate particle agglomeration and growth.^{1,2,4,9,10,17} Such reversible transformations between different metal species induced by varying reaction conditions have been explored in several studies for Rh on ZSM-5 for methane oxidation to methanol,¹⁸ redispersion of SnO₂ clusters in BEA-zeolites during ketone oxidation,¹⁹ Pt cluster formation from isolated atoms in Y zeolite during ethane dehydrogenation,²⁰ high-temperature (>750 K) oxidations on single-site Pt and Pt clusters in high silica CHA^{2,9,21} and MFI,^{13,22} and hydrothermal treatments of Pd nanoparticles with air and steam in MFI, MWW, and CHA zeolites.²³⁻²⁶

Here, we extend previous models for interconversion between cations and nanoparticles^{26–32} to redispersion of Pt particles in zeolites by analyzing the influence of the initial Pt particle size distribution and environmental conditions on the interconversion between Pt particles and cations. We used density functional theory (DFT) calculations to determine the most stable Pt²⁺ cation structures and use free energy approximations for supported and unsupported nanoparticles^{33–35} to estimate the size-dependent energies of encapsulated Pt particles in CHA zeolites. We combine these cation and particle energies at different particle sizes and environmental conditions (P_{O_2} , P_{H_2O} , P_{H_2} , T) to develop thermodynamic phase diagrams for Pt speciation within the zeolite. The phase diagrams demonstrate that at low temperatures, at large initial particle size distributions, and under hydrating and reducing conditions, conversion from Pt particles to cations is negligible. Conversely, high temperature and oxidizing conditions favor cation formation, consistent with experimental data reported at the same conditions. The thermodynamic models were then extended to BEA, TON, and MFI zeolites and validated with experimental literature reports. Ostwald ripening (OR) kinetic Monte Carlo (kMC) simulations show that the supported particle free energy model best describes experimentally observed interconversion kinetics for Pt-CHA, and model parameterization suggests van der Waals-induced stabilization of Pt particles.

4.2 Methods

4.2.1 DFT and AIMD Calculations

We used the Vienna ab initio simulation package³⁶(VASP, version 5.4.4) to perform spin-polarized periodic, plane-wave calculations with an energy cutoff of 400 eV and projected augmented wave (PAW) method for core-valence interactions.^{37,38} We used the 12 and 24 T-site 1Al and 2Al Pd-exchanged structures in SSZ-13 (CHA) from Mandal et al.,³⁹ with the Pd atoms replaced by Pt atoms, and bulk Pt, α -PtO₂ (space group: p-3m1), and Pt₃O₄ (space group: Pm-3n) structures reported in the Materials Project database⁴⁰ as initial guesses and optimized the structures with the Perdew-Becke-Ernzerhof (PBE) functional,⁴¹ followed by the Heyd-Scuseria-Erzenhof (HSE06)^{36,41-46} functional. For the Pt and Pt-oxide bulk structures, we used the kpoint mesh detailed in the Materials Project database,⁴⁰ and for the zeolite structures, we used only the Γ point. We used self-consistent field (SCF) electronic energies and atomic forces convergence criteria of 10^{-8} eV and 0.01 eVÅ⁻¹ for calculations with the PBE functional and of 10^{-6} eV and 0.03 eVÅ^{-1} for calculations with the HSE06 functional. We incorporated dispersion corrections for all calculations with the Becke-Johnson damping (D3(BJ)-vdw) method.^{42,43} To further optimize the SSZ-13 structures beyond their local minima, we used spin-polarized ab initio molecular dynamics (AIMD) simulations. The 60 ps NVT simulations (Nose-Hoover thermostat), with 0.5 fs time steps, began with the local energy minima optimized structure and were run at 298 K with the PBE functional and D3(BJ)-vdw corrections. We then optimized the five lowest energy structures from the AIMD simulation's trajectories with PBE, followed by HSE06, and used the resulting lowest energy structure of the five for our thermodynamic calculations. All optimized geometries are provided in the CONTCARS attachment in the Supporting Information.

4.2.2 Ab Initio Free Energy Calculations

We calculated the 0 K energies, relative to bulk Pt, for cation species with O_2 and H_2O -based ligands and bulk oxide species using Eqs 1 and 2, respectively. Likewise, we used Eqs 3 and 4 to calculate relative free energies. For a given species, ZPE represents the zero point vibrational energies and S^{vib} represents the vibrational entropies, both of which are derived from the calculated species frequencies. Frequencies were calculated for gas-species (H_2O , O_2 , H_2), bulk Pt metal and metal-oxides, and CHA cation and framework species. We assumed that the frequencies for cations in other zeolite frameworks (TON, BEA, MFI) are comparable to those in CHA and thus used the CHA frequencies to calculate the free energies of all zeolite frameworks. The term ΔS^{ST} (Eq 5) accounts for the translational and rotational entropy difference between bare and ligand-covered Pt in the zeolite framework. This value was calculated using the Sackur-Tetrode equation, assuming that adsorbates retain $\approx 2/3$ of their gas-

phase translational entropy.^{47,48} $M_{x,y}$ in the Sackur-Tetrode equation is the mass of the ligand(s) bonded to Pt. $\Delta \mu_i$ (Eq 6) represents the difference in chemical potential between 0 K and the environmental conditions for gas species i, where P^o is the standard state pressure (1 atm).^{49,50} Gas species chemical potentials were calculated using the NIST JANAF thermochemical tables.⁵¹

$$\Delta E_{x,y}^{form} = E_{Z*PtH_xO_y} - E_{Pt_{bulk}} - \frac{x}{2} \left(E_{H_2O} - \frac{1}{2} E_{O_2} \right) - \frac{y}{2} E_{O_2}$$
(4.1)

$$\Delta E_{\mathrm{Pt}_{a}\mathrm{O}_{b,\,\mathrm{bulk}}}^{form} = \frac{E_{\mathrm{Pt}_{a}\mathrm{O}_{b,\,\mathrm{bulk}}}}{a} - E_{\mathrm{Pt}_{\mathrm{bulk}}} - \frac{b}{a} \left(\frac{E_{\mathrm{O}_{2}}}{2}\right) \tag{4.2}$$

$$\Delta G_{x,y}^{form}(T, \Delta \mu_{O_2}, \Delta \mu_{H_2O}) = \Delta E_{x,y}^{form} + ZPE_{x,y} - T\left(\Delta S_{x,y}^{ST}(T) + \Delta S_{x,y}^{vib}(T)\right) -\frac{x}{2}\left(\Delta \mu_{H_2O} - \frac{1}{2}\Delta \mu_{O_2}\right) - \frac{y}{2}\Delta \mu_{O_2}$$
(4.3)

$$\Delta G_{\mathrm{Pt}_{a}\mathrm{O}_{b,\,\mathrm{bulk}}}^{form}(T,\Delta\mu_{\mathrm{O}_{2}}) = \Delta E_{\mathrm{Pt}_{a}\mathrm{O}_{b,\,\mathrm{bulk}}}^{form} + ZPE_{\mathrm{Pt}_{a}\mathrm{O}_{b,\,\mathrm{bulk}}} - T\left(\Delta S_{\mathrm{Pt}_{a}\mathrm{O}_{b,\,\mathrm{bulk}}}^{\mathrm{vib}}(T)\right) - \frac{b}{2a}\Delta\mu_{\mathrm{O}_{2}}$$

$$(4.4)$$

$$\Delta S_{x,y}^{\rm ST} = (E_{\rm Z*PtH_{x}O_{y}} - E_{\rm Z*Pt}) \approx \frac{2}{3} k_{\rm B} \ln \left[\left(\frac{2\pi M_{x,y} k_{\rm B} T}{h^{2}} \right)^{3/2} \left(\frac{k_{\rm B} T}{P^{\rm o}} \right) \frac{e^{5/2}}{N_{\rm A}} \right]$$
(4.5)

$$\Delta\mu(P,T) = \mathrm{R}T\ln\left(\frac{P}{\mathrm{P}^{\mathrm{o}}}\right) \tag{4.6}$$

Similar to Eqs 4.1 and 4.2, Eqs 4.7 and 4.8 represent the 0 K energy and free energy of Z_2Pt under reducing conditions (in H_2), respectively, relative to Pt bulk:

$$\Delta E_z^{form} = E_{Z_*PtH_z} - E_{Pt_{bulk}} - \frac{z}{2} E_{H_2}$$
(4.7)

$$\Delta G_z^{form}(T, \Delta \mu_{\mathrm{H}_2}) = \Delta E_z^{form} - T \left(\Delta S_z^{\mathrm{ST}}(T) + \Delta S_{\mathrm{Pt}}(T) \right) - \frac{z}{2} \Delta \mu_{\mathrm{H}_2}$$
(4.8)

To derive the equilibrium fraction of ion-exchanged Pt $(n_{\rm Pt}/N_{\rm Pt})$ at a given pressure, temperature, and initial particle size, we minimized the free energy of the cationparticle system ($\Delta G_{\rm sys}$) with respect to the amount of ion-exchanged Pt $(n_{\rm Pt})$. Eqs 9-11 gives the free energy of the system assuming the ion exchange enthalpy is coverageindependent:

$$\Delta G_{sys.}(P,T,d) = n_{\rm Pt} \left(\Delta \bar{G}_{x,y}^{form}(T) - \Delta \bar{G}_{\rm particle}^{form}(T) \right) - T \Delta S_{config.}$$
(4.9)

$$\Delta \bar{G}_{\text{particle}}^{form}(P,T,d) = \frac{\sum_{i=\text{Pt},\alpha-\text{PtO}_2,\text{Pt}_3\text{O}_4} \left(\Delta G_i \exp\left(\frac{-\Delta G_i}{\text{R}T}\right)\right)}{\sum_{i=\text{Pt},\alpha-\text{PtO}_2,\text{Pt}_3\text{O}_4} \left(\exp\left(\frac{-\Delta G_i}{\text{R}T}\right)\right)}$$
(4.10)

$$\Delta \bar{G}_{x,y}^{form}(P,T,d) = \frac{\sum_{i=Z_2 Pt, Z_2 Pt(H_2 O)_2} \left(\Delta G_i \exp\left(\frac{-\Delta G_i}{RT}\right)\right)}{\sum_{i=Z_2 Pt, Z_2 Pt(H_2 O)_2} \left(\exp\left(\frac{-\Delta G_i}{RT}\right)\right)}$$
(4.11)

Here, $\Delta \bar{G}_{\text{particle}}^{form}(P, T, d)$ is the Boltzmann averaged free energy (relative to bulk Pt) of each particle species $(i = \text{Pt}, \alpha - \text{PtO}_2, \text{ and Pt}_3\text{O}_4)$ computed using Eq.18 or Eq.19. Similarly, $\Delta \bar{G}_{x,y}^{form}(P, T, d)$ is the Boltzmann averaged free energy (relative to bulk Pt) of the cationic species $(i = \text{Z}_2\text{Pt} \text{ and } \text{Z}_2\text{Pt}(\text{H}_2\text{O})_2)$ with their respective x, y values as denoted in Eq.4.1. The configurational entropy of cationic species in the zeolite lattice $(\Delta S_{config.})$ is excluded when calculating $\Delta \bar{G}_{x,y}^{form}(P,T,d)$ and treated separately in Eq 4.9. The number of configurations for ion-exchanged Pt is computed as a function of $\frac{N_{\text{Pt}}}{N_{2\text{Al}}} = \frac{\text{Total number of Pt atoms in the system}}{\text{Total number of exchange sites}}$ (Eq. S1 and S2) and the expression was then simplified using Stirling's approximation (Eq. S3) to obtain $\Delta S_{config.}$. Minimizing $\Delta G_{sys.}$ with respect to the amount of ion-exchanged Pt (n_{Pt}) gives the fraction of cationic species at equilibrium (Eq 12):

$$X_{\text{cation,tot}}(P,T,d) = \frac{n_{\text{Pt}}}{N_{\text{Pt}}} = \frac{\sqrt{(\phi+1)^2 f^2 + 4\phi(1-f)f} - (\phi+1)f}{2(1-f)\phi}$$
(4.12)

where the Boltzmann factor partitioning free energies of particles and cationic species in the system is denoted as f(P, T, d)

$$f(P,T,d) = \exp\left(\frac{-(\Delta \bar{G}_{x,y}^{form} - \Delta \bar{G}_{\text{particle}}^{form})}{\mathbf{R}T}\right)$$
(4.13)

and ϕ is defined as the ratio between total number of Pt atoms in the system to the total number of 2Al pairs available for ion exchange:

$$\phi = \frac{N_{\rm Pt}}{N_{\rm 2Al}} = \frac{\text{Total number of Pt atoms in the systyem}}{\text{Total number of exchange sites}}$$
(4.14)

To calculate the fraction of Pt for each different species, we used the Boltzmann factors associated with each species and mass conservation (Eqs 15-16):

$$X_{\text{cation},i}(P,T,d) = \frac{X_{\text{cation,tot}} \exp\left(\frac{-\Delta G_i}{RT}\right)}{\sum_{i=Z_2 \text{Pt}, Z_2 \text{Pt}(H_2 \text{O})_2} \left(\exp\left(\frac{-\Delta G_i}{RT}\right)\right)}$$
(4.15)

$$X_{\text{particle},i}(P,T,d) = \frac{\left(1 - X_{\text{cation,tot}}\right) \exp\left(\frac{-\Delta G_i}{RT}\right)}{\sum_{i=\text{Pt},\alpha-\text{PtO}_2,\text{Pt}_3\text{O}_4} \left(\exp\left(\frac{-\Delta G_i}{RT}\right)\right)}$$
(4.16)

4.2.3 Pt Particle Size-Dependent Models

For calculating Pt metal and Pt-oxide surface energies, we used the Python Materials Genomics (Pymatgen) package. We used the built-in Slabgenerator function^{52–54} to construct symmetric slabs, with Miller indices of $1 \leq$, for Pt, α -PtO₂, and Pt₃O₄ from their respective, optimized bulk structure. The slabs were 10 Å in thickness and had a 12 Å vacuum space to avoid periodic interactions between surfaces in the z-direction. To calculate the energies of these structures, we scaled the k-point mesh in the x and y directions by the ratio of the bulk to slab dimensions in the x and y directions, respectively. The k-point mesh in the z direction was set to one. We optimized the Pt and Pt_3O_4 slab structures with the PBE-D3(BJ)-vdw functional, using the same convergence criteria used with the bulk structures, to minimize computational expense. We chose to compute relative surface energies for α -PtO₂ with the HSE06-D3(BJ)-vdw functional to ensure that the calculated surface energies were not negative (which is an issue for α -PtO₂ specifically) and remained physically reasonable over all conditions. We calculated the surface energy (γ_{slab}) of each facet with Eq 4.17:⁵⁵

$$\gamma_{\rm slab}(P_{\rm O_2}, T) = \frac{E_{\rm slab} - n_{\rm bulk} E_{\rm bulk} - n_{\rm O} \mu_{\rm O}(P_{\rm O_2}, T)}{2A} \tag{4.17}$$

where n_{bulk} represents the number of units of the bulk structure and n_{O} represents the number of O atoms, in excess or deficit of the bulk units, in the slab, μ O is the chemical potential of O, A is the surface area of one face of the slab, E_{slab} is the total, DFT-calculated energy of the slab, and E_{bulk} is the energy of one unit of the relevant bulk structure. We calculated the equilibrium average surface energies (γ_{avg}) and shape factors (η) of the Pt metal and oxides by using Pymatgen's Wulffshape function to generate their respective Wulff constructions.⁵⁶ With the input of γ_{slab} for each species' facets, the function outputs the average surface energies and shape factors at a range of μ_{O} values. At the conditions we explored μ_{O} ranges from -9.3 to -4.1 eV.

To calculate the effect of particle size-dependence on free energy, we examined thermodynamic predictions with both supported and unsupported free energy model corrections. The supported model (Eq 4.18), based on calorimetric measurements of metals on oxide supports and developed by Campbell et al., describes the free energy, relative to the bulk free energy of formation, for a supported hemispherical particle of diameter $d.^{33,57,58}$ Here, d is the effective diameter, such that the d of a metal oxide particle is equal to the diameter of a Pt metal particle comprised of an equivalent number of Pt atoms. In addition, $E_{adh.}(P_{O_2}, T)$ is the adhesion energy between a particle and support, and ρ is the volume per mole of metal or metal oxide. Eq 4.18 reduces to Eq 4.20 when $E_{adh.}(P_{O_2}, T)$ is approximated with the Young-Laplace equation (Eq. 4.19), where θ is the contact angle between the spherical cap-like particle on a flat support. In the absence of a known $E_{adh.}$ for the Pt metal and oxide particles supported on the zeolite, we considered $\theta = 60^{\circ}$, 90°, and 120° to represent a range of adhesion strengths (Fig. A2.1). The lack of variance in thermodynamic predictions between the different angles allowed us to select $\theta = 90^{\circ}$ for the remaining thermodynamic calculations.

$$\Delta G_{\rm sup}(d, P_{\rm O_2}, T) = (3\gamma_{\rm avg}(P_{\rm O_2}, T) - E_{\rm adh.}(P_{\rm O_2}, T))(1 + \frac{1.5 \text{ nm}}{d})(\frac{2\rho}{d})$$
(4.18)

$$E_{\text{adh.}}(P_{O_2}, T) = \gamma_{\text{avg}}(P_{O_2}, T)(1 + \cos\theta)$$
 (4.19)

$$\Delta G_{\rm sup}(d, P_{\rm O_2}, T) = \gamma_{\rm avg}(P_{\rm O_2}, T)(2 - \cos\theta)(1 + \frac{1.5 \text{ nm}}{d})(\frac{2\rho}{d})$$
(4.20)

The unsupported model (Eq 4.21), based on work by Sun et al., describes the free energy, relative to the bulk free energy of formation, for an unsupported spherical particle, of effective diameter d, in a vacuum.^{35,54} For this model, at d > 2 nm, the free energy is described by a Gibbs-Thomson-like equation. At d < 2 nm, we used the PBE-D3(BJ)-vdw functional to optimize and calculate the energies of Pt particle structures from Ignatov et al.⁵⁹ up to 260 Pt atoms (≈ 2 nm). These energies were interpolated using a cubic spline to determine ΔG_{interp} , which provides free energy estimates for any particles with d < 2 nm. The piecewise nature of ΔG_{unsup} corrects for the shape factor and average surface energy dependence on particle size at d < 2 nm (Fig. A2.2).²⁸

$$\Delta G_{\text{unsup}}(d, P_{\text{O}_2}, T) = \begin{cases} G_{\text{interp}}(d) & , d < 2\text{nm} \\ \\ \eta \gamma_{\text{avg}}(P_{\text{O}_2}, T)(\frac{2\rho}{d}) & , d > 2\text{nm} \end{cases}$$
(4.21)

To generate thermodynamic predictions, we calculated the fraction of a given Pt species in the system with the size-corrected ΔG values.

4.2.4 Modeling Gas-phase Mediated Kinetics for Pt Redispersion

To model the redispersion of Pt metal to ion-exchanged Pt^{2+} , we used the kinetic theory of gases and collision theory. The monomers are generated via a gas phase OR process (Eq 4.22), and the process is modeled via Eq 23.

$$\operatorname{Pt}_{k} + \operatorname{O}_{2} \longleftrightarrow \operatorname{PtO}_{2}(g) + \operatorname{Pt}_{k-1}$$

$$(4.22)$$

A monomer ejected from the surface of a Pt particle may either bind to another Pt particle or exchange as a Pt ion at a Z_2H_2 site. Therefore, we represent the competitive redispersion kinetics of the Pt-zeolite system by coupling Eqs 4.23 and 27. In Eq 4.24, K_{OS} is the pre-exponential factor for OR, Ck is the concentration of particles (per nm⁻²) comprised of k Pt atoms, and A_k is the exposed surface area of the same particle. The sticking coefficient (S) of monomers was assumed to be 1 when calculating K_{OS} (Eq 4.22), and $m_{PtO_2(g)}$ is the molecular mass of $PtO_2(g)$.

$$\frac{dC_k}{dt} = \begin{cases} -K_{\rm OS}C_kA_k(P_b - P_k) + K_{\rm OS}C_{k-1}A_{k-1}(P_b - P_{k-1}) &, P_k < P_b \\ 0 &, P_k = P_b \\ K_{\rm OS}C_kA_k(P_b - P_k) - K_{\rm OS}C_{k+1}A_{k+1}(P_b - P_{k+1}) &, P_k > P_b \end{cases}$$
(4.23)

$$K_{\rm OS} = \frac{S}{\sqrt{2\pi m_{\rm PtO_2(g)} \mathbf{k}_{\rm B} T}} \tag{4.24}$$

Depending on how the equilibrium monomer pressure of a particle (P_k) compares to the background monomer (PtO_2) pressure (P_b) of the particle ensemble, the given particle will grow $(P_k < P_b)$ or shrink $(P_k > P_b)$.^{26,60,61} Considering PtO₂(g) mass conservation, P_b is given by the weighted average (by total exposed area) of equilibrium particle pressures:⁶⁰

$$P_b = \frac{\sum_k A_k n_k P_k}{\sum_k A_k n_k} \tag{4.25}$$

where n_k is the number of Pt particles comprised of k atoms per surface area, and P_k is the pressure of $PtO_2(g)$ in equilibrium with a Pt particle comprised of k atoms at a given oxygen pressure. P_k is the product of oxygen partial pressure P_{O_2} and the equilibrium constant between $PtO_2(g)$ and the Pt particle (Eq 4.26), which depends on the formation energy of the $PtO_2(g)$ monomer ($\Delta G_{\text{monomer}}^{form}$), and the free energy of the particle.

$$P_{k} = P_{O_{2}} \exp\left(\frac{-\Delta G_{\text{monomer}}^{form} + \Delta G(d, P_{O_{2}}, T)}{k_{B}T}\right)$$
(4.26)

The collision frequency between gas monomers and atom-trapping (Z_2H_2) sites is given by,

$$\frac{d\theta_{\rm Z_2Pt}}{dt} = \frac{(1 - \theta_{\rm Z_2Pt})P_bS}{N_0\sqrt{2\pi m_{\rm PtO_2(g)}k_{\rm B}T}}$$
(4.27)

which describes the change in the fraction of occupied atom-trapping sites with time.²⁶ In Eq 4.27, θ_{Z_2Pt} is the fraction of trapping sites occupied with Pt, S is the sticking coefficient, and N_0 is the density of trapping sites (per nm⁻²). We evaluated N_0 by assuming spherical CHA crystallites with a diameter of 50 nm and Si/Al = 8.5, consistent with the data reported by Moliner et al.,² a random Al distribution, and a framework density for CHA of 15.1 T atoms per 1000 Å³. The monomer formation free energy term ($\Delta G_{\text{monomer}}^{form}$) will be different for the supported or unsupported Pt nanoparticle free energy models (Eq. 4.18 and 4.21). A sample code for the simulations is provided as a Supporting Information attachment file.

To simulate redispersion kinetics under different conditions, we first generated three unsupported (assuming spherical particles) and five supported (assuming hemispherical particles) log-normally distributed (LND) particle size distributions (Tables A3.1 and A3.2) consistent with the initial Pt-Pt coordination number of 7.36 (Fig A3.1) observed experimentally by Moliner et al.² Subsequently, we solved the system of differential equations defined by Eqs 23 and 27 using kMC. As kMC is a stochastic method, we averaged 20 independent simulations to obtain predictions. Fig. A3.2 demonstrates that the kMC simulations converge by 20 iterations. Using the kMC simulations for particle's supported and unsupported free energy models, we explored two types of temperature behaviors that correspond to the specific experiments reported by Moliner et al.² The first temperature behavior was a temperature ramp from 293 K to 773 K, at a rate of 10 K min⁻¹. The second behavior was sequential isothermal treatments (373, 473, and then 773 K), each held for 120 minutes before stepping to the next temperature. From the simulations, we obtained the extent of ion exchange and particle size distributions as a function of time and calculated the average Pt-Pt coordination number. To calculate the coordination number from the number of atoms in the particle, we interpolated the number of Pt atoms in a particle and the Pt-Pt coordination number reported by de Graaf et al.⁶² We used the MATLAB tool GRABIT⁶³ to extract the initial particle size distribution, the extent of conversion over time, and Pt-Pt coordination numbers from Moliner et al.² Finally, we compare those experimental observations with our simulation results.

4.2.5 Details of Zeolite Structure Sampling

To sample possible CHA (36 T-site supercell), BEA (64 T-site supercell), and TON (48 T-site supercell) Pt zeolite structures, we generated initial Z_2Pt and Z_2H_2 structures based on the pure silica form of the zeolite supercells from the international zeolite association (IZA) database. We repeated IZA zeolite unit cells until each cell vector was greater than 10 Å to avoid self-interactions between atoms due to periodic effects. From these supercells, we generated all possible two Al configurations (Z_2) within 10 Å. To determine the symmetrically unique Z_2 configurations, we used a connectivity-based graph isomorphism test using Python NetworkX code,⁶⁴ similar to prior work.⁶⁵ All configurations with Al-O-Al were removed because according to Löwenstein's Rule,^{66,67} Al-O-Al bond formation in zeolites is unlikely. The Pt and H atoms, for the Z_2Pt and Z_2H_2 structures, respectively, were placed inside the zeolite rings using vector Eqs 28⁶⁸ and 29:⁶⁹

$$\mathbf{Al} - \mathbf{Cu} = (\mathbf{Al} - \mathbf{O}_1) + (\mathbf{Al} - \mathbf{O}_2) \tag{4.28}$$

$$\mathbf{H} - \mathbf{O} = \frac{(\mathbf{O} - \mathbf{T}_1) + (\mathbf{O} - \mathbf{T}_2)}{|(\mathbf{O} - \mathbf{T}_1) + (\mathbf{O} - \mathbf{T}_2)|} \times 0.98$$
(4.29)

Here, O_1 and O_2 are the position vectors of oxygen atoms bound to the same Al, and T_1 and T_2 are position vectors of T-site atoms bound to the same O. These equations

place Pt in the plane generated by $Al-O_1$ and $Al-O_2$, and H atoms on the plane generated by $O-T_1$ and $O-T_2$,⁶⁹ with an O-H distance of 0.98 Å. Once we placed the Pt and H atoms, we performed another graph isomorphism test to remove any similar structures. We optimized the remaining structures with the PBE-D3(BJ)vdw functional, followed by the HSE06-D3(BJ)-vdw functional. Our calculations for CHA and TON showed that the low energy Z₂Pt and low energy Z₂Cu structures reported in previous studies⁶⁵ have analogous coordination to the zeolite framework. Therefore, based on previously reported Z₂Cu structures for BEA,⁶⁵ we only sampled eight candidate minimum energy Z₂Pt structures.

4.3 Results and discussion

4.3.1 Pt cation speciation in CHA zeolites

We identified the lowest energy Pt cation structure in CHA zeolites (Fig. 1a) by considering structures with either one Al ("Z") or two Al ("Z₂") T-sites with different Al pair configurations, and ligands. For the 1Al exchange site, all T-site positions for Al in CHA are crystallographically equivalent, therefore all ZPt sites are the same. For the two Al exchange sites, we computed the relative energies of Z_2Pt structures with different Al pair configurations (Fig. A1.1). The lowest energy Z_2Pt zeolite structure, similar to other ion-exchanged Pt-group metals like Cu,⁷⁰ and Pd,³⁹ contains a Pt²⁺ cation populating a six-membered ring (6MR) with two Al separated by two Si atoms (third nearest neighbor [3NN] configuration; Fig. 1b), similar to the lowest energy structures reported for Cu and Pd exchange in CHA zeolites.^{39,70} We next calculated energies for different numbers of H- and O- ligands

attached to the ionic Pt atoms in the Z₂Pt and ZPt structures (Fig. 2a, b). To determine the Pt species that are most thermodynamically stable at a given set of environmental conditions, we first calculated the 0 K energies for all the cationic Pt motifs considered (Z_{*}PtH_xO_y; *=1-2) using the HSE06 functional with D3(BJ)vdw dispersion correction, and then used thermodynamic correlations detailed in Section 2.2 to compute the Gibbs free energies (ΔG^{form}) of these structures relative to Z₂Pt as a function of T, P_{O_2} , and P_{H_2O} . A comparison of $\Delta G^{form}(T, P_{O_2}, P_{H_2O})$ for all Z_{*}PtH_xO_y species shows that Z₂Pt, along with H₂O-solvated Z₂Pt (Z₂Pt(H₂O)_{x=2,4}), are the most stable conformers over a wide range of conditions (Fig. 1b, 2a, and A2.3). More specifically, the Z₂Pt and Z₂Pt(H₂O)₂ structures persist as the most stable Pt zeolites structure under all temperatures and environmental conditions of interest for interconversion between cations and nanoparticles⁶⁰(T > 550 K, $P_{H_2O}/P_{O_2} < 0.5$ at $P_{O_2} = 20$ kPa).



Figure 4.1: (a) Framework of CHA with cutout of cage, comprised of four, six, and eight member rings, from a periodic supercell and (b) the HSE06-D3(BJ)vdw-optimized structures of the most stable Pt/CHA species.



Figure 4.2: (a) Phase diagram of the most stable Pt/CHA species at different pressures and temperatures. The dotted line represents the boundary of the conditions of interest for interconversion. (b) Free energies of $Z_{(1-2)}$ PtH_xO_y species at 10 kPa H₂O and 20 kPa O₂ for 550 K (blue) and 773 K (red).

4.3.2 Thermodynamics of Interconversion between Pt particles and Pt Cations

Under oxidizing conditions, our computational model consists of competing reactions that convert Pt metal into oxides (α -PtO₂, Pt₃O₄) (Eqs. 4.30 and 4.31, respectively) and ion-exchange reactions that convert metal and oxide particles to Z₂Pt cations (Eqs.4.32-4.35):

$$Pt_{bulk} + O_2 \longleftrightarrow \alpha - PtO_2 \tag{4.30}$$

$$Pt_{bulk} + \frac{4}{3}O_2 \longleftrightarrow \frac{1}{3}Pt_3O_4$$
(4.31)

$$Pt_{bulk} + Z_2H_2 + \frac{1}{2}O_2 \longleftrightarrow Z_2Pt + H_2O$$
(4.32)

$$\alpha - \operatorname{PtO}_{2\operatorname{bulk}} + \operatorname{Z}_{2}\operatorname{H}_{2} \longleftrightarrow \operatorname{Z}_{2}\operatorname{Pt} + \operatorname{H}_{2}\operatorname{O} + \frac{1}{2}\operatorname{O}_{2}$$

$$(4.33)$$

$$\frac{1}{3}\operatorname{Pt}_{3}\operatorname{O}_{4}_{\text{bulk}} + \operatorname{Z}_{2}\operatorname{H}_{2} \longleftrightarrow \operatorname{Z}_{2}\operatorname{Pt} + \operatorname{H}_{2}\operatorname{O} + \frac{1}{6}\operatorname{O}_{2}$$

$$(4.34)$$

$$Pt_{bulk} + Z_2 H_2 \longleftrightarrow Z_2 Pt + H_2$$

$$(4.35)$$

We next computed the relative stability of the species in Eqs 4.30-4.34 (Section 2.2) by evaluating ΔG^{form} at the conditions of interest (550 and 773 K, maximum $P_{\rm H_2O}/P_{\rm O_2} = 0.5$), relative to Pt_{bulk} using HSE06-D3(BJ)vdw computed energies. The computed formation energies for the Pt-oxide species (Table A2.1, Fig. A2.4), derived from Eqs. 4.30 and 4.31, are consistent with experimental and computational values reported in the literature.⁷¹⁻⁷⁴

The energies of Pt and Pt-oxides are sensitive to nanoparticle size. We estimated the size-dependent energy of Pt metal and Pt-oxide nanoparticles using two different models: supported and unsupported particles. These models bookend two extremes for calculating particle free energies. The supported model (ΔG_{sup} ; Eq 4.18), which was developed by Hemmingson and Campbell, is consistent with calorimetry measurements of oxide-supported nanoparticles³³ and describes metal particles adhered to a support (the zeolite in this instance) by stabilizing nanoparticle energies relative to cations through the contribution of the adhesion energy. We previously used this model to estimate the free energy of Pd nanoparticles supported on the external surface of zeolite crystallites.²⁶ This adhesion energy is absent in the unsupported model (ΔG_{unsup} ; Eq 4.21), which was developed by Sun et al.^{34,35} and considers the metal particles to be in vacuum and is similar to the Gibbs-Thomson equation. In Pt-zeolites, Pt particles may be located on the external surface of the zeolite cryst

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tallites or encapsulated within the zeolite pores,⁷⁵ which contain framework oxygen atoms that provide multiple weak points of contact to stabilize particles via van der Waals forces instead of requiring direct adhesion to the framework. Here, we considered both models and compared them to experimental studies to ascertain the model that best describes these systems and determine how encapsulation modulates nanoparticle energies.

Fig. 3 reports the resulting phase diagrams that show the equilibrium fraction of Pt atoms that form Pt metal particles, Pt-oxide particles, and Pt cations, represented by green, blue, and red, respectively, for a range of P_{O_2} , P_{H_2O} , P_{H_2} , T, and particle size distributions. Both the supported and unsupported free energy models demonstrate that under dry conditions ($P_{H_2O}/P_{O_2} = 5e^{-4}$), Pt cations are the most thermodynamically stable species over nearly the entire range of temperatures and particle sizes (Fig. 3a). This trend largely persists at increasing water pressure ($P_{H_2O}/P_{O_2} = 0.50$, Fig. 3b). In contrast, upon exposure to H₂, which promotes the reduction of Pt-oxide particles and Pt cations to Pt metal,^{4,13,17} only small particles (< 5 nm) at extremely high temperatures (> 1100 K) favor conversion to cations (Fig. 3c). At 4 kPa H₂, both models predict complete conversion to Pt metal particles at all particle sizes for temperatures below 923 K. This complete thermodynamic reversibility between Pt cations and metal particles (< 923 K) through exposure to O₂ and H₂ is consistent with experimental observations at these conditions.^{2,9}

Both of the free energy models predict results for Pt cation interconversion that are consistent with experimental reports,² with only slight discrepancies between each other. Under wet conditions, at low temperatures (< 700 K) and large, initial average particle sizes (> 10 nm), both the unsupported and supported models predict a percentage (maximum of 32% and 53%, respectively, at 100 nm and ≈ 610 K) of



Figure 4.3: Pt particle size and temperature-dependent thermodynamic phase diagram for the conversion of Pt particles to Pt species in CHA at (a) $P_{\rm H_2O} = 0.01$ kPa and $P_{\rm O_2} = 20$ kPa, (b) $P_{\rm H_2O} = 10$ kPa and $P_{\rm O_2} = 20$ kPa, and (c) $P_{\rm H_2} = 4$ kPa. The top and bottoms rows represent predictions for the unsupported and supported free energy models, respectively. (d) Color key that denotes red, green, and blue as Pt cations, Pt metal, and Pt-oxides, respectively.

Pt-oxide particles, however, Pt-oxides are more pronounced in the supported model. Similarly, under exposure to H_2 , smaller Pt metal particles persist at higher temperatures in the supported model. This difference is the consequence of the unsupported model treating large particles in vacuum as less stable relative to particles supported on the zeolite.³³ Both models predict 100% conversion to cations at most oxidizing conditions, including at an average initial particle size of 1.5 nm at 773 K, under dry conditions, which is consistent with experimental data from Moliner et al. at these conditions.² Model predictions that the addition of H_2 at 673 K favors full reversibility back to Pt particles are also in agreement with Moliner et al.,² further suggesting that both of our models appear to accurately represent the thermodynamics of interconversion in CHA zeolites.

4.3.3 Extending CHA Thermodynamic Model to Other Zeolite Topologies

To demonstrate the generalizability of the two free-energy models to other zeolite topologies, we examined the predicted thermodynamics for the BEA, TON, and MFI frameworks. Each of these zeolites has a minimum energy Pt cation structure (see Section 2.5 for details of structure sampling) similar to that of CHA. The Pt cation structure of MFI is the same as Z_2Pt structure in CHA, consistent with EXAFS data and DFT calculations from Felvey et. al.,²² with a Pt²⁺ cation in a 3NN 6MR 2Al configuration. The IR spectra of Pt ion-exchanged MFI and BEA also contain T-O-T stretching frequencies consistent with a Pt²⁺ cation in a 6MR 2Al site,²² and sampling different Al-pair configurations (Fig. A1.2a) indicates that the most stable cation structure is Pt2+ charge-compensating 3NN 6MR 2Al sites. The Z₂Pt 6MR 2Al site is the most stable cation location for CHA, BEA, MFI, and TON (Fig. A1.2b). Thus, we only consider adsorbate-free Z₂Pt 6MR 2Al sites for modeling the thermodynamics of the BEA, TON, and MFI zeolites.

Using the most stable cation structures for each of the zeolite frameworks and their associated ion-exchange energies (and $\frac{N_{2A1}}{N_{A1}}$ values consistent with experimentally synthesized materials²²), we developed phase diagrams for the unsupported (Fig. 5) and supported (Fig. A2.9) Pt free-energy models. Analogous to the thermodynamic results for CHA, the models largely predict complete conversion to cations under dry and wet conditions for each of the zeolite topologies (Fig. 5, A2.9). Exposure to H₂ results in the formation of thermodynamically stable Pt particles at low temperatures. At higher temperatures and smaller particle sizes, each zeolite topology has different degrees of ion-exchange (Fig. 5, A2.9). The structural difference between zeolites likely impacts conversion to Pt cations through changes in ring strain and distortion in CHA (Fig. A2.10), BEA, MFI, and TON (Fig. 5c, f, i). Ring expansion due to ion-exchange, associated with more exothermic ion-exchange energies, results in more thermodynamically favorable Pt cation species.^{22,69,76–78} Conversely, the more endothermic Pt exchange energy for CHA (Fig. S10) is associated with ring contraction.

These thermodynamic predictions for each zeolite are consistent with a number of experimental observations. Pt particles in MFI have been reported to undergo complete particle redispersion at 20% O_2 and 923 K, and subsequent exposure to 10% H_2 at 773 K results in Pt particle formation.²² Both of these observations for MFI are consistent with the supported particle and unsupported particle model predictions over the range of modeled particle sizes. Across the range of modeled particle sizes, the thermodynamic predictions for BEA at 20% O2 and 873 K also agree with experimental results that demonstrate the majority of Pt clusters in BEA redisperse to Z_2Pt after exposure to these conditions.²² The overall thermodynamic consistency of both the unsupported and supported free-energy models across the four different zeolite frameworks indicates that while both models are useful for estimating the conditions alone are incapable of discerning the more accurate free energy model for encapsulated Pt nanoparticle energies.



Figure 4.4: Pt particle size (using the unsupported particle free energy model, results for the supported model are shown in Fig. A2.9) and temperature-dependent thermodynamic phase diagrams for the conversion of Pt particles to Pt cations in (a, b) BEA ($N_{\rm Pt}/N_{\rm Al} = 0.021$, $N_{\rm 2Al}/N_{\rm Al} = 0.08$), (d, e) MFI ($N_{\rm Pt}/N_{\rm Al} = 0.036$, $N_{\rm 2Al}/N_{\rm Al} = 0.04$), and (g, h) TON ($N_{\rm Pt}/N_{\rm Al} = 0.039$, $N_{\rm 2Al}/N_{\rm Al} = 0.05$). The diagrams (a, d, g) are calculated at $P_{\rm H_2O} = 10$ kPa and $P_{\rm O_2} = 20$ kPa, and (b, e, h) $P_{\rm H_2} = 10$ kPa. Zeolite structures show the 6 MR ring distortions from the Z₂H₂ frameworks (H atoms hidden for clarity) to ion-exchanged structures for (c) BEA, (f) MFI, and (i) TON. The exchange energies of Pt atoms in each zeolite framework under exposure to O₂ and H₂O ($\Delta E_{x,y}^{form}$) and H₂ (ΔE_z^{form}) are listed under the respective framework's structure.

4.3.4 Kinetics of Interconversion of Pt particles to Ion-exchanged Pt Cations

The thermodynamic predictions for both supported and unsupported free energy models are consistent with reported experimental data;^{2,22} therefore, our next aim is to discern the model that best describes the redispersion kinetics of encapsulated Pt nanoparticles to Pt cations. To describe the kinetics of Pt redispersion, our kinetic model assumes an Ostwald ripening (OR) mechanism (Eqs. 4.23, 4.27) to generate gas phase monomers that exchange between nanoparticles (analogous to the model developed by Plessow et al.⁶⁰), coupled with reaction of monomers at Z_2H_2 ion-exchange sites in the zeolite (Scheme 1).²⁶ In OR, particles disintegrate to generate mobile monomers (Eq 4.22), which under the conditions considered here are mobile, neutral, gas-phase $PtO_2(g)$.⁷⁹ The gaseous monomers can traverse the zeolite and migrate to either other Pt particles, facilitating particle growth, or monomers may travel to and exchange at atom-trapping sites, which are the 2Al sites that exchange Pt to form Z_2Pt cations at the conditions of interest (negligible P_{H_2O} , 20 kPa O_2). At these conditions, we assume that ion exchange is an irreversible process because equilibrium is heavily shifted towards cations at all temperatures, which is consistent with our thermodynamic predictions in Fig. 3a. To model the redispersion process, we simulated a two-step mechanism where the Pt metal particles eject monomers that compete to form either larger Pt metal particles or ion-exchanged Pt^{2+} (Scheme 1).

To model time-dependent ion-exchange at different temperatures, we simulated the Pt particle-zeolite system (Scheme 1) using kMC with constrained parameters (Table 1). The parameters included the monomer formation energy ($\Delta G_{\text{monomer}}^{form}$) and nanoparticle surface energy ($\gamma_{\text{avg,Pt}}$) for the unsupported particle model and the entire



Scheme 4.1: Proposed scheme for unsupported and supported Pt particle redispersion and sintering, facilitated via gas-phase mediated Ostwald ripening with atom trapping sites.

 $(3\gamma_{\text{avg,Pt}} - E_{\text{adh}})$ term in the supported particle model. The average particle size (\bar{x}) and the standard deviation $(s_{\bar{x}})$ of LND (consistent with TEM) particle size distributions were constrained (Fig A3.1) to satisfy the initial Pt-Pt coordination number of 7.36 ± 1.4 reported by Moliner et al.² In the absence of energy estimates of $\gamma_{\text{avg,Pt}}$ and $\Delta G_{\text{monomer}}^{form}$ for zeolite-encapsulated particles, and precise initial particle size distribution data, we searched for parameter sets ($\gamma_{\text{avg,Pt}}$ or ($3\gamma_{\text{avg,Pt}} - E_{\text{adh.}}$), $\Delta G_{\text{monomer}}^{form}$, \bar{x} , and $s_{\bar{x}}$) starting with initial guesses consistent with surface energies for Pt nanoparticles in the absence of the zeolite framework: $\gamma_{\text{avg,Pt}} = 96 \text{ meVÅ}^{-2}$ (DFT-computed), $E_{\text{adh.}} = \gamma_{\text{avg,Pt}}^{80}$ and $\Delta G_{\text{monomer}}^{form=1.69}$ eV.⁶⁰ The parameter ranges explored in the kinetics simulations resulted in negligible variations (Fig. A2.5-2.8) of thermodynamic predictions with both free energy models (Eq.18 and 21). First, we fit the kinetic model parameters by minimizing the sum of squared errors between the predicted and experimentally reported extent of atoms in Pt particles converted to Z₂Pt in Pt-CHA (grey points in Fig. 5a) during a linear temperature ramp from 293 to 773 K at 10 K min⁻¹ in 20 kPa O_2 .² Next, we validated these regressed kinetic model parameter sets by comparing the simulated average Pt-Pt coordination numbers under sequential isothermal holds at 373, 473, and 773 K to the Pt-Pt coordination numbers from EXAFS reported in the same study² (Fig. 5b).

Parameter	Value
$\overline{{}^{1}S}$	1
$^{2}N_{0}$	$1.98 \times 10^8 \text{ nm}^{-2}$
${}^{2}P_{O_{2}}$	20 kPa
$^{3}\gamma_{\rm avg,Pt}$: for unsupported	$40 - 105 \text{ meV}\text{Å}^{-2}$
$^{3}(3\gamma_{\text{avg,Pt}} - E_{\text{adh.}})$: for supported	$110 - 210 \text{ meV}\text{\AA}^{-2}$
$^{3}\Delta G_{\mathrm{monomer}}^{form}$	1.30 - 1.85 eV
$^3\bar{x}$	0.5 - 1.5 nm
${}^3S_{ar{x}}$	$0.18 - 0.48 \ nm$

¹ Parameter value from Plessow et al.⁶⁰

 2 Parameter value from Moliner et al. 2

³ Ranges of considered values for parameters.

 Table 4.1: Parameters used for gas-mediated ion-exchange mechanism.

Fig. 5a reports the best fit parameters for the fraction of Pt converted to Z_2Pt over time (grey points are experimental data). The kinetic model predictions for different particle size distributions (Table A3.1 and A3.2) were explored using a grid search of $\gamma_{avg,Pt}$ (or $3\gamma_{avg,Pt} - E_{adh}$ in the supported particle model) and $\Delta G_{monomer}^{form}$ (Tables A3.3-10) during parameter fitting, and are shown in Fig. A3.6 and A3.7. The surface energy, $\gamma_{avg,Pt}$, and the monomer formation free energy, $\Delta G_{monomer}^{form}$, primarily influence the initial rate of interconversion. For example, either a higher $\gamma_{avg,Pt}$, or a lower $\Delta G_{monomer}^{form}$, result in higher rates of PtO₂(g) monomer formation, leading to faster initial ion exchange (Fig. A3.3). The initial particle size distributions, each consistent with the experimental average Pt-Pt coordination number,² control the slope of the interconversion curve (Fig. A3.4 and A3.5).



Figure 4.5: Kinetic model predictions (using kMC) for the (a) extent of ion-exchange with the temperature ramp and (b) Pt-Pt coordination numbers for the isothermal hold simulations. Purple ($\bar{x} = 0.75$ nm) and orange ($\bar{x} = 1.25$ nm) traces are the best-fit unsupported and supported free energy models, respectively. The grey points are experimental data from Moliner et al..²

With the best-fit parameters, both the supported and unsupported models produce comparable accuracy (Table A3.3-3.10) for kinetic predictions (Fig. 5a) and validations (Fig. 5c). The distributions with $\bar{x} = 0.5$ and 0.75 nm for the unsupported particle free energy model and $\bar{x} = 0.75$, 1.25 nm for the supported particle free energy model predict Pt redispersion during the temperature ramp within a typical error for time-resolved XANES fitting ($\pm 10\%$ each datapoint).⁸¹ For each of these particle size distributions (PSD), we validated regressed parameter sets (Fig. A3.8 and A3.9) and found that $\bar{x} = 0.75$ nm ($\gamma_{\text{avg,Pt}} = 75 \text{ meVÅ}^{-2}$, $\Delta G_{\text{monomer}}^{form} = 1.65 \text{ eV}$) and $\bar{x} = 1.25$ nm ($3\gamma_{\text{avg,Pt}} - E_{\text{adh.}} = 160 \text{ meVÅ}^{-2}$, $\Delta G_{\text{monomer}}^{form} = 1.69 \text{ eV}$) best predict
the average Pt-Pt coordination numbers (Fig. 5c) for the unsupported and supported models, respectively. However, the initial PSD of the best supported particle model is consistent with the reported TEM particle size distribution (and not just the avg. particle size estimated from EXAFS)² (Fig. A3.10d), while the unsupported model deviates significantly from this distribution (Fig. A3.10g). Therefore, we conclude that the supported particle model with the fit parameters above provides the best consistency with experimental data.



Figure 4.6: (a) Separated Pt(100) and hydroxylated silica slab, and (b) the change in adhesion energy $(E_{adh.})$ between Pt on silica vs the average distance between surface Pt atoms and surface O atoms (on the silica slab). Non-surface atoms that were constrained in DFT optimizations are depicted with low opacity in (a).

In the best (supported particle) model, the regressed $\Delta G_{\text{monomer}}^{form}$ is equivalent to that for Pt nanoparticles on other supports,^{60,61} suggesting that the energy cost to eject a gas monomer from a Pt nanoparticle is not sensitive to zeolite encapsulation of the particle. To decouple the energy contributions of the regressed ($3\gamma_{\text{avg,Pt}} - E_{\text{adh.}}$) value, we computed the distance-dependent interaction energy between a silica slab (as an approximate model for a high silica zeolite) and a Pt surface (Fig. 6a). The hydroxylated silica β -cristobalite (001) slab represents the internal or external zeolite surface, and the Pt(100) surface was used to represent Pt particles due to a minimal lattice mismatch with the silica slab. This is a rough approximation that does not account for several other factors that could influence the effective adhesion energy between Pt and the zeolite, such as the degree of hydroxylation of the silica slab^{82,83} and the exact surface structure of the particle. Fig. 6b shows that the attraction between Pt and the silica surface results in an adhesion energy of 24 meVÅ⁻² at an ideal Pt-silica slab distance (2.5 Å). Using this computed $E_{\rm adh}$ and the regressed ($3\gamma_{\rm avg,Pt} - E_{\rm adh}$.) value in the best-fit model, the $\gamma_{\rm avg,Pt}$ is 61 meVÅ⁻². Therefore, the average Pt surface energy deviates considerably from those in the absence of a zeolite where $\gamma_{\rm avg,Pt}$ is 96 meVÅ⁻². This difference in surface energy is likely due to a combination of stability imparted by zeolite encapsulation and (or) reduction in the surface energy via oxygen binding, as suggested by Plessow et al.⁶⁰ These results suggest that zeolite encapsulation slows down the rate of monomer formation in OR due to the lower $\gamma_{\rm avg,Pt}$. Consequently, zeolite encapsulation imparts additional stability for Pt nanoparticles in comparison to other common oxide supports.

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Chapter 5

Thermodynamic Limit of Nanoparticle Disintegration in the Presence of Atom-trapping Sites.

This chapter describes a theoretical treatment of the thermodynamics of supported nanoparticle redispersing into mononuclear (single atom or cationic) species. The manuscript for this work is currently in preparation (Wijerathne, A.; Paolucci, C. Thermodynamic Limit of Nanoparticle Disintegration in the Presence of Atomtrapping Sites , *In Preparation*).

5.1 Introduction

Losing surface atoms from supported metal particles due to sintering is a prevalent issue in catalysis, especially for applications such as Diesel Oxidation Catalysts (DOC) where catalysts are exposed to harsh reaction conditions (10% H₂O, \approx 1073 K and residual air). To combat metal sintering, various strategies such as encapsulating metal particles,¹⁻⁵ increasing the metal support interaction strength by modifying the support,² and alloying^{4,6} are proposed in literature. The most common mode of deactivation is Ostwald ripening (OR) mediated by mobile atomic species. These mobile atomic species are ejected from metal particles and facilitate sintering by travelling from smaller particles to bigger particles due to local concentration gradients.^{7–9} However, if the support has a large number of atomic environments (referred to as trapping sites: Scheme 5.1) that can capture and trap the mobile metal species, Jones et al.¹⁰ showed that these mobile metal species could be beneficial for maintaining a high surface area of metal particles by isolating single atoms or small atomic clusters, and prevent particle sintering. In their study, $\rm Pt/La\text{-}Al_2O_3$ is physically mixed with ceria (CeO_2) powder to increase the number of trapping sites, and the results showed that depending on the morphology of ${\rm CeO}_2$ crystallites, sintering decreased or stopped because of complete disintegration of Pt particles to Pt single atoms. Later, Goodman et al.¹¹ observed the same phenomenon of metal nanoparticles disintegrating into single atoms for 0.007%wt. Pd/Al₂O₃, causing deactivation of the methane oxidation catalysts, where single atoms are inactive. However, for high Pd loading (0.659% wt.) of the same $\rm Al_2O_3$ support, a lower degree of deactivation was observed. Importantly, Pd particle sintering was the dominant process of deactivating high Pd loading catalysts, in which particle disintegration was minimal. Goodman et al.¹¹ qualitatively explain those variations in degree of particle disintegration using statistical mechanics arguments.

Atom trapping has been used as a promising approach to design highly dispersed metal (Fe, Pt, Pd, Au, Ru, and Rh) atoms on various supports such as CeO_2 , Al_2O_3 , zeolites, and N doped graphene.^{12–17} However, almost a decade after Jone's experimental observations¹⁰ and five years after Goodman's analysis,¹¹ a comprehensive theoretical study on atom trapping and its implications on particle growth, is still lacking. Here, we theoretically investigate a general system consisting of metal nanoparticles and trapping sites using a statistical mechanics approach. Then, we used numerical

simulations to test the validity of our findings.



Initial system (1): All trapping sites are empty

Scheme 5.1: Schematic representation of two states of the system of metal nanoparticles supported on a trapping site containing support. Two states of the system are, (1) no metal atoms in the trapping sites and, (2) some metal atoms that left the particles are trapped in the trapping sites.

5.2 Theoretical treatment of thermodynamics of atom-trapping

Suppose that the initial system consists of $N_{\rm M}$ number of metal atoms (M= Pd, Pt, Ru, Rh, etc.) in the nanoparticles, and $N_{\rm trap}$ is the number of trapping

sites on the support which are accessible for the metal atoms (Scheme 5.1-system1). This initial system represents experimental procedures that follow a physical mixing of nanoparticles with the support and subsequent thermal treatment to disperse nanoparticles..^{10,11} One trapping site can only trap a single M atom. As a first approximation, we assume all the M atoms in the particle state are energetically equivalent (potential energy= $E_{\rm M}$ per M atom) and Gibbs free energy of the initial system (G_1):

$$G_1 = N_{\rm M} E_{\rm M} + N_{\rm trap} E_{\rm vacancy} - T(S_{\rm particles1} + S_{\rm vacancies1})$$
(5.1)

where E_{vacancy} is the energy of a vacant trapping site, T is the temperature, and $S_{\text{particles1}}$ and $S_{\text{vacancies1}}$ are the configurational entropies of particle and vacancy ensembles in the initial system respectively.

Consider another system with $n_{\rm M}$ metal atoms trapped in the support and $(N_{\rm M} - n_{\rm M})$ metal atoms remaining in the particles (Scheme 5.1-system2). Assuming all trapping sites have similar M binding energies, the Gibbs free energy of this system (G_2) :

$$G_{2} = (N_{\rm M} - n_{\rm M})E_{\rm M} + (N_{\rm trap} - n_{\rm M})E_{\rm vacancy} + n_{\rm M}E_{\rm M, \ trapped \ in \ vacancy} - T(S_{\rm particles2} + S_{\rm vacancies2})$$

$$(5.2)$$

where, $E_{\rm M, trapped in vacancy}$ is the energy of the trapping site containing a single M atom trapped in it. The free energy change from the initial state (1) to the final state (2) in the system is given by,

$$\Delta G_{\rm sys} = G_2 - G_1 \tag{5.3}$$

Substituting equation 5.1 and 5.2 to 5.3, we get,

$$\Delta G_{\rm sys} = n_{\rm M} \Delta E_{\rm bind} - T(\Delta S_{\rm particles} + \Delta S_{\rm vacancies}) \tag{5.4}$$

and, the energy of M binding to a trapping site (ΔE_{bind}) is defined as the reaction energy of the following atom exchange process:

$$M_{(\text{in particles})} + \text{Vacancy} \longrightarrow M_{(\text{trapped in vacancy})}; \Delta E_{\text{bind}}$$
 (5.5)

To include the effect of reaction conditions (T, P, gas concentrations) to the binding energy, we replace ΔE_{bind} in equation 5.4 with ΔG_{bind} , where ΔG_{bind} is the Gibbs free energy for an atom trapping in an isolated vacancy site with the reaction shown in equation 5.5.

$$\Delta G_{\rm sys} = n_{\rm M} \Delta G_{\rm bind} - T (\Delta S_{\rm particles} + \Delta S_{\rm vacancies}) \tag{5.6}$$

Note that we subsume all entropic contributions (at constant T) except the configurational entropy contributions to ΔG_{bind} term because 0 K DFT calculations and free energy approximations such as NIST-JANAF thermochemical tables¹⁸ commonly used in the field do not account for configurational entropy effects. However, entropic effects may play a critical role and have been proposed as the major driving force for atom trapping in systems where atom trapping reactions are energetically uphill.¹¹ Therefore, we treated configurational entropy terms separately in the following section.

For a given number of trapped M atoms (n_M) , multiple combinations of trapping sites on the support are available for atom trapping, giving rise to the configurational entropy term $S_{\text{vacancies}}$. Statistically, all these configurations are equally likely and viable microstates of the system. The initial system has only one configuration for vacancies where all trapping sites are empty and for any reasonably sized $(n_{\rm M}, N_{\rm trap} \gg$ 1) system, $S_{\rm vacancies2} \gg S_{\rm vacancies1} = 1$. This simplifies the configurational entropy change as, $\Delta S_{\rm vacancies2}$.

The entropy due to particle ensembles are represented by $S_{\text{particles}}$ and a higher entropy should be expected from non-uniform particle distributions (equation 5.5), where large number of particle fractions(x_i , i = the number of atoms in the particle) contribute to the entropy.^{19,20}

$$S_{\text{particles}} = -N_{\text{M}}k_{\text{B}}\sum_{i=1}^{i_{max}} x_i \ln x_i$$
(5.7)

The total number of metal atoms $(N_{\rm M})$ is conserved during the exchange (equation 5.5), and $S_{\rm particles}$ do not depend on the absolute size of particles (equation 5.7) but depends on the size differences. Therefore, we assume that $\Delta S_{\rm particles} \approx 0$ as both initial and final systems may have a large number of particles with different sizes. This approximation is expected to hold for most systems except for systems with zero metal particles.

These two assumptions ($\Delta S_{\text{vacancies}} \approx S_{\text{vacancies}2}$ and $\Delta S_{\text{particles}} \approx 0$) simplifies the equation 5.6 to the following:

$$\Delta G_{\rm sys} = n_{\rm M} \Delta G_{\rm bind} - T S_{\rm vacancies2} \tag{5.8}$$

where $S_{\text{vacancies2}}$ is the configurational entropy of the M-trapped and the remaining empty vacancies.

To estimate the $S_{\text{vacancies2}}$, we consider the microstates of the system consistent with the constraints in the system-2: n_{M} M atoms in trapping sites, N_{M} total M atoms, and N_{trap} total trapping sites. Each trapping site can either exchange one M atom, or remain vacant. For the number of trapped M atoms n_{M} , the total number of configurations in the trapping site lattice is given by the product between the number of ways for choosing n_{M} number of M atoms out of N_{M} total Pt atoms, and from vacancies, choosing n_{M} trapping sites out of N_{trap} . Therefore, the total number of configurations ($\Omega_{\text{vacancies2}}$) for atom trapping is given by,

$$\Omega_{\text{vacancies2}} = \binom{N_{\text{M}}}{n_{\text{M}}} \times \binom{N_{\text{trap}}}{n_{\text{M}}}$$
(5.9)

By definition, the configurational entropy of the trapping sites is,

$$S_{\text{vacanicies2}} = k_{\text{B}} \ln \left[\binom{N_{\text{M}}}{n_{\text{M}}} \times \binom{N_{\text{trap}}}{n_{\text{M}}} \right]$$

= $k_{\text{B}} \ln \left(\frac{N_{\text{M}}!}{(N_{\text{M}} - n_{\text{M}})!n_{\text{M}}!} \frac{N_{\text{trap}}!}{(N_{\text{trap}} - n_{\text{M}})!n_{\text{M}}!} \right)$ (5.10)

Applying Stirling's approximation, $S_{\text{vacanicies}2}$ can be simplified to,

$$S_{\text{vacanicies2}} = k_{\text{B}} \left[N_{\text{M}} \ln(N_{\text{M}}) - (N_{\text{M}} - n_{\text{M}}) \ln(N_{\text{M}} - n_{\text{M}}) \right]$$

+ $k_{\text{B}} \left[N_{\text{trap}} \ln(N_{\text{trap}}) - (N_{\text{trap}} - n_{\text{M}}) \ln(N - n_{\text{M}}) - 2n_{\text{M}} \ln(n_{\text{M}}) \right]$ (5.11)

Substituting equation 5.11 to 5.8 gives:

$$\Delta G_{\rm sys} = n_{\rm M} \Delta G_{\rm bind} - k_{\rm B} T \left[N_{\rm M} \ln(N_{\rm M}) - (N_{\rm M} - n_{\rm M}) \ln(N_{\rm M} - n_{\rm M}) \right] -k_{\rm B} T \left[N_{\rm trap} \ln(N_{\rm trap}) - (N_{\rm trap} - n_{\rm M}) \ln(N_{\rm trap} - n_{\rm M}) - 2n_{\rm M} \ln(n_{\rm M}) \right]$$
(5.12)

As $n_{\rm M}$ (the number of M exchanged into the trapping sites) varies, $\Delta G_{\rm sys}$ also

changes. The minimum ΔG_{sys} corresponds to the minimum in free energy of the system and, therefore, the thermodynamic equilibrium. At equilibrium,

$$\frac{\partial \Delta G_{\rm sys}}{\partial n_{\rm M}} = 0 \tag{5.13}$$

Using equation 5.12 and 5.13, we get:

$$\frac{\Delta G_{\text{bind}}}{k_{\text{B}}T} = \ln\left(\frac{(N_{\text{trap}} - n_{\text{M}})(N_{\text{M}} - n_{\text{M}})}{n_{\text{M}}^2}\right)$$
(5.14)

We then solve equation 5.14 for $n_{\rm M}/N_{\rm trap}$ to evaluate the fractional exchange of M atoms to the trapping sites. Rearranging 5.14 :

$$\left(\frac{n_{\rm M}}{N_{\rm trap}}\right)^2 (1-f) + \left(\frac{n_{\rm M}}{N_{\rm trap}}\right) (\phi+1)f - \phi f = 0$$

with, $f = \exp\left(\frac{-\Delta G_{\rm bind}}{k_{\rm B}T}\right)$ and, $\phi = \frac{N_{\rm M}}{N_{\rm trap}}$ (5.15)

Equation 5.15 is a quadratic formula in $\left(\frac{n_{\rm M}}{N_{\rm trap}}\right)$ that has two roots. However, only one of those roots satisfies the physical constraint set by the maximum number of M atoms in the closed system: $0 \le \left(\frac{n_{\rm M}}{N_{\rm M}}\right) \le 1$. The valid root is given by the equation 5.16.

$$\left(\frac{n_{\rm M}}{N_{\rm trap}}\right) = \frac{\sqrt{(\phi+1)^2 f^2 + 4(1-f)\phi f} - (\phi+1)f}{2(1-f)}$$
(5.16)

Equation 5.16 has a singularity at f = 1, corresponding to a system with 0 binding free energy. However, the solution from equation 5.16 converges to the expected root of equation 5.15 with f = 1 as $f \rightarrow 1$, indicating that the physical system does not have a jump discontinuity in the solution as seen for processes such as phase transformations.^{21,22} Using equation 5.16 we evaluate the equilibrium fraction of M atoms trapped in vacancies (X_{trapped}) as follows:

$$X_{\text{trapped}} = \left(\frac{n_{\text{M}}}{N_{\text{M}}}\right) = \frac{\sqrt{(\phi+1)^2 f^2 + 4(1-f)\phi f} - (\phi+1)f}{2\phi(1-f)}$$
(5.17)

Equation 5.17 describes the thermodynamic limit of atom trapping within our stipulated assumptions above.

Goodman et. al^{11} analysed atom trapping in a system similar to Scheme 5.1 for their Pd on Al_2O_3 samples. Using the same terms described above, their approximated form of the thermodynamic limit for atom trapping is given by equation 5.18:

$$X_{\text{trapped}} = \left(\frac{n_{\text{M}}}{N_{\text{M}}}\right) = \frac{f}{f + \phi} \tag{5.18}$$

Equation 5.18 has a different functional form than equation 5.17 we previously obtained.



Figure 5.1: The equilibrium fraction of M atoms in trapping sites computed using, (a) equation 5.17 and (b) equation 5.18 for different support compositions and binding energies (ϕ and f).

To compare two solutions (equation 5.17 and equation 5.18), we computed the

equilibrium fraction of M atoms trapped in vacancies (X_{trapped}) using both equations (Figure 5.1) for different support compositions (ϕ) and M binding energies (f). Both solutions indicate that exergonic binding energies (f > 1) and excess trapping sites (ϕ < 1), in most cases, lead to the complete disintegration of nanoparticles to form single atoms in the trapping sites (e.g., point C). However, if the binding energy is weakly exergonic (ΔG_{bind} closer to 0 but < 0), then the configurational entropy drives a small extent (< 0.5) of metal atoms to particles despite the exothermic binding energy. Further, both equations converge to the same solution if f = 1, i.e., when $\Delta G_{\text{bind}} = 0$ (e.g. point A). However, the two solutions significantly deviate from each other in the first quadrant (e.g., point B), which is representative of systems with exergonic binding energies (f > 1) and a limited amount of trapping sites compared to M atoms in particles ($\phi > 1$). Physical constraint $n_{\rm M} \leq N_{\rm trap}$ indicates that such systems' maximum fraction of atom trapping, $X_{\text{trapped, max}} = 1/\phi$ is limited by the number of trapping sites, despite favorable trapping reaction energies. However, the solution from equation 5.18 fails to capture this phenomenon and predicts fractions higher than this maximum (Figure 5.1 b). In contrast, the solution from equation 5.17remains within the physically feasible region, as indicated by the vertical contours (i.e. X_{trapped} is limited by ϕ) in the first quadrant of Figure 5.1 a. The X_{trapped} evaluated for the third and fourth quadrants (points D and E, respectively) using two equations show a qualitative agreement, although equation 5.18 shows higher sensitivity to ϕ and f parameters as indicated by the narrower color strips in these regions of the heatmap (Figure 5.1 a,b - lower half).

5.3 Numerical simulations to evaluate thermodynamics of atom-trapping

To verify the equilibrium fraction of trapped M atoms, X_{trapped} estimated by our thermodynamic model, we simulated a system with M particles and trapping sites. To keep the model simple, we assumed that all M particles are the same size and have a single type of M monomer ejecting/binding site on the particle. This assumption may not hold for a practical system with a wide distribution of particle sizes where the energy of a metal atom (\propto cohesive energy) is higher in smaller particles.^{23,24} Additionally, each particle's atoms that are located in terraces, corners, and edge sites have different coordination numbers and energies. Different types of trapping sites with varying trapping reaction energies could trap M atoms. However, we assumed homogeneous trapping sites. These two assumptions considerably simplify the simulations and also enable us to directly compare the X_{trapped} estimated from equations.

To numerically estimate the equilibrium fraction of atoms in the trapping sites (X_{trapped}) for each scenario A-D, we used the Metropolis Monte Carlo (MC) algorithm, shown in Scheme 5.2 on appropriate model systems (n_{M} number of M atoms, N_{trapped} number of trapping sites, and f). The model system can take any size and any initial condition consistent with ϕ and f parameters. In this simulation, we used 600 M atoms in particles and accordingly calculated the required empty $N_{\text{trapped}} = \phi/n_{\text{M}}$. Then, we randomly pick one metal atom from the particles and one trapping site out of N_{trapped} , and attempt to swap their states. If the system energy lowers with the proposed swap, we accept the move; else, we accept the swap move according to the Boltzmann criterion (Scheme 5.2). After a sufficient number of MC moves, the



Scheme 5.2: Monte Carlo sampling algorithm to simulate the equilibrium properties (at temperature T) of metal nanoparticle-trapping site system.

system's statistical properties do not change with swap moves, and the sampled microstate properties can be averaged to estimate macroscopically expected properties.



Figure 5.2: Energy of the system per metal atom and the step-averaged fraction of M in trapping sites (X_{trapped}) evaluated using Metropolis Monte Carlo simulations ($T = 800 \text{ K}, n_{\text{M}} = 600$) of the two-state system for, parameters corresponds to (a) point B and (b) point D. Solid red and blue dash-dotted lines show systems initiated with all M atoms in particles and 20% M atoms in trapping sites, respectively.

Figure 5.2 shows the variation of the system energy (per M atom) and the averaged X_{trapped} with the number of MC moves for two systems with exergonic (system B) and endergonic (system D) ΔG_{bind} values. While steps in Metropolis MC are not time steps, and therefore, details such as the rates of trapping reactions and the time the system takes to reach the equilibrium state cannot be calculated, it is a powerful technique to find the equilibrium state of a system. In system B, the atom trapping lowered the energy as expected ($\Delta G_{\text{bind}} < 0$), but reached equilibrium at $X_{\text{trapped}} = 0.32$ due to insufficient amount of trapping sites to exchange more M into trapping sites. System D at equilibrium ($X_{trapped} = 0.35$) approximately has the same fraction of M atoms trapped as in the equilibrated system B. However, enthalpy drives the equilibration of system B, whereas entropy predominantly drives system D due to the large number of trapping sites. A similar scenario of entropy driven particle disintegration is reported for Pd/Al₂O₃ by Goodman et. al.¹¹ With increasing system size, we observe a decrease in fluctuations of system properties (such as energy), and the number of MC steps required to achieve equilibrium increases. However, regardless of the system size, the same equilibrium is reached. We simulated systems with the same ϕ and f parameters and different initial conditions as denoted in red and blue in Figure 5.2. Despite differences in initial condition, the same equilibrium state is reached, suggesting that the system has only one equilibrium state. This observation is consistent with the governing equation 5.15.



Figure 5.3: Comparison of analytical solution of, (a) equation 17 and (b) equation 18 to the step-averaged fraction of M in trapping sites (X_{trapped}) evaluated using Metropolis Monte Carlo simulations (T = 800 K). Purple data points (A-E) correspond to the points shown in Figure 5.1 and data in the Table 5.1.

Next, we compare the equilibrium X_{trapped} from numerical solutions for each system (A-E) to the values estimated from the two equations (Figure 5.3). Equation 5.17 gives the same equilibrium X_{trapped} as the numerical simulations while, the solution in equation 5.18, proposed by Goodman et.al.¹¹ qualitatively agrees with the numerical solutions, except for system B. In system B, the estimation from equation 5.18 deviates considerably from the numerical solution, suggesting that the equilibrium in some systems is not captured correctly.

Data point in Figure 5.1	ϕ	f	$\begin{array}{c} \Delta G^*_{\rm bind} \\ (\rm kJ\ mol^{-1}) \end{array}$	$X_{ m trapped}$ Eqn-5.17	X_{trapped} from MC	$X_{ m trapped}$ Eqn-5.18	X_{trapped} max. possible
А	1	1	0	0.50	0.50	0.50	1
В	3	14	-17.5	0.32	0.32	0.82	0.33
\mathbf{C}	0.2	2	-4.6	0.90	0.90	0.90	1
D	0.1	0.02	26.0	0.35	0.35	0.17	1
Ε	3	0.3	8.0	0.19	0.19	0.09	0.33

*Calculated for T = 800 K using the value of f. i.e. $\Delta G_{\text{bind}} = -\text{R}T \ln(f)$.

Table 5.1: Calculated and simulated fraction of trapped M for data points (A-E) in Figure 5.1.

5.4 Conclusions and future work

Thermodynamic analysis of atom trapping reveals the key limiting factors for atom trapping processes as (1) the relative density of trapping sites compared to the metal loading of the system and (2) the atom trapping reaction free energy. Moreover, our analysis gives a physically acceptable solution for various scenarios that were overlooked in previous studies. Our approximation of all metal atoms (M) in particles having the same energy breaks down for smaller (< 2 nm) nanoparticles as M atoms in smaller particles are, on average, more under-coordinated and, therefore, higher in energy than those in larger particles. Although, a simple analytical expression cannot be derived for the X_{trapped} without this approximation, the numerical simulation we implemented can be adapted to the size (and/or shape) dependent energies of metal atoms on particles. Currently, we are expanding the numerical simulation, including additional free energy-driven atom exchange processes such as Ostwald ripening (OR) that could simultaneously occur in a practical system.

In the current model, we computed exchange free energy using an isolated trapping site; however, adsorbate-adsorbate interactions can change ΔG_{bind} , especially at high metal/trapping site ratios ($\phi \approx 1 \text{ or } \phi > 1$). For future investigations, the impact of these interactions on the equilibrium can be explored. Some supports, such as zeolites, are known to have a heterogeneous mix of trapping sites, and these may be required in the numerical model to make quantitatively accurate predictions for such systems. Despite these inherent model limitations, we anticipate that our analysis readily applies to different systems with atom trapping, paving ways to design and optimize the sinter-resistant single-atom catalysts.

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Chapter 6

Effects of Treatment Conditions and Support Properties on the Sintering Kinetics of Palladium Nanoparticles.

This chapter is a paper currently in preparation (Bolton, K. B.; Wijerathne, A.; Rosenberger, J.; Ahn S. H.; Swann, W.; Getsoin A. B.; Li, C.W.; Paolucci, C.; and Gounder, R. Effects of Treatment Conditions and Support Properties on the Sintering Kinetics of Palladium Nanoparticles, *In Preparation*). This work focuses on understanding how the sintering rate of Pd supported on alumina is influenced by initial particle size distribution, support properties, and gas environment. To study how the initial particle size distribution influence sintering, Li group and Gounder group at Purdue synthesized Pd nanoparticles of different average particle sizes and distributions (normally and log-normally distributed with similar averages) on various amorphous Al_2O_3 supports (γ - Al_2O_3 , La-doped Al_2O_3 , and $\theta\delta$ - Al_2O_3) using incipient wetness impregnation and colloidal synthesis. Then, Pd particle size as a function of gas treatment time was quantitatively characterized by TEM, O_2 chemisorption, and C_2H_4 hydrogenation. As the co-first author of the paper in preparation, I contributed
to the computational modeling of Pd sintering using Ostwald ripening models and collected part of the experimental data during my six-month stay at Purdue University.

6.1 Introduction

Gasoline-powered combustion engines produce emissions consisting of carbon monoxide (CO, 0.5 vol.%), unburned hydrocarbons (HC, ca. 350 ppm), nitrogen oxides (NO_x, ca. 900 ppm), hydrogen (H₂, 0.17 vol.%), water (H₂O, 10 vol.%), carbon dioxide (CO₂, 10 vol.%), oxygen (O2, 0.5 vol.%), and nitrogen.¹ The amounts of CO, HC, and NO_x in automotive exhaust are governmentally regulated because they pose significant health and environmental concerns.² Therefore, three-way catalysts (TWC) were developed for gasoline vehicles to simultaneously convert these criteria pollutants (NO_x, CO, HC) into environmentally benign products (CO₂, N₂, H₂O). TWCs commonly consist of precious metals (Pt,³ Pd,⁴ and/or Rh^{5,6}) supported on alumina or ceria and coated on monolithic substrates having a honeycomb structure. During vehicle operation, TWCs experience a wide range of operating conditions that cause changes to the metal exposed surface area, oxidation state, and surface coverage, leading to decreased reaction rates and overall catalyst lifetime.⁷ Furthermore, supported noble metal catalysts have been shown to undergo deactivation processes, commonly metal sintering decreasing the exposed surface area, leading to decreased conversion (per surface metal) for their desired applications and limiting the catalyst lifetime.^{8–10}

On Pd-supported materials, the initial particle size,¹¹ post-deposition treatment temperature,^{12,13} gas environment,^{14–17} and support^{18,19} have been reported to result in different sintering rates. For Pd/Al_2O_3 catalysts, Kang et al.,¹¹ reported the slowest sintering rates after cyclic aging $(3\% \text{ O}_2 \text{ or } 3\% \text{ CO}, 10\% \text{ CO}_2, 10\% \text{ H}_2\text{O}, \text{ and balance})$ N_2) at 1173 K for the particles (4 – 17 nm) with the largest initial average diameters. Similarly, Richardson et al. studied rates of sintering of Ni supported on silica under He from 673 – 873 K with different initial metal particle size distributions and showed average particle size and the type of size distribution can affect the metal sintering rates.^{20,21} Chen et al.¹² reported increasing temperature (823 - 1273 K) under lean $(10\% H_2O, 16\% O_2, 10\% CO_2, balance N_2)$ or rich $(10\% H_2O, 1\% H_2, 8\% CO_2, balance N_2)$ N_2) continually decreases the Pd dispersion, where rich conditions resulted in higher sintering rates. Therefore, depending on the gas environment, Pd particles may form intermediates such as $Pd(CO)_2$, oxidize to form PdO, or form Pd-hydrides.^{15,16} In H₂containing environments, the formation of unstable β -palladium hydride species has been reported, and accelerated sintering rates were observed on silica,¹⁷ indicating the strong dependency of the gas environment on Pd sintering. In addition, Rodriguez et al.¹⁸ found Pd supported on gamma alumina (γ -Al₂O₃), silica (SiO₂), and zirconia (ZrO_2) resulted in a similar extent of sintering in oxygen below 1073 K, where PdO was observed when increasing to 598 K and these further converted to metallic Pd when the temperature was heated further to 1023 K. However, Cao et al.¹⁹ observed different extents of sintering in Pd supported on γ -Al₂O₃ and Ce_{0.5}Zr_{0.5}O₂ (CZ) under different gas environments (i.e., air, H_2 , or N_2). Interestingly, the Pd/CZ material was observed to sinter minimally under air conditions due to strong metal support interactions (i.e., strong Pd-O-Ce bonds), but sintering was not inhibited under H₂ or inert environments. By contrast, the Pd/γ -Al₂O₃ sintered significantly (>100 nm) regardless of the gas environment. Although these support material properties and gas environment conditions have been shown to influence sintering rates, their impact on the sintering mechanism is unknown.

Supported metal particles (e.g., Pd^{14,22}) typically sinter via one of two mechanisms, which prevail under different conditions of metal-support interaction, gas pressures, and temperature. In the Ostwald ripening (OR) mechanism, molecular (e.g., mononuclear) intermediates are exchanged between larger particle aggregates through surface-mediated or vapor-mediated transport routes, while in the particle migration and coalescence (PMC) mechanism, smaller particles move on the surface to encounter other metal domains and form larger particles. However, if the metalsupport interaction is strong, the OR mechanism of sintering will prevail.²³ From in situ TEM, Hansen et al. did not observe overlapping of neighboring metal particles at moderate temperatures (up to 973 K), leading the authors to conclude the contribution of particle coalescence for sintering in Pd and Ni is minimal.¹⁴ Also, Lardinois et al. showed at low (<973 K) temperatures, surface-mediated OR is the dominant sintering mechanism for Pd sintering because the vapor pressure of Pd monomers is negligible $(3.2 \times 10^{-16} \text{ kPa})$ compared to more volatile oxides such as PtO₂ $(2.8 \times 10^{-8} \text{ kPa})$ kPa) that are known to facilitate gas-phase mediated sintering.¹³ High temperatures (>1173 K) in an oxidizing environment²² can facilitate volatile Pd monomer formation (e.g., $Pd(OH)_2$ or PdO), increasing the sintering rate via gas-phase mediated OR due to the order of magnitude increase in the number of Pd monomers emitted.²⁴ However, the alumina support itself can undergo slow sintering to decrease its available surface area under such high-temperature conditions, convoluting Pd particle sintering rate measurements. Therefore, this study explores sintering at T = 1073K, where the γ -Al₂O₃ surface area is relatively stable,²⁵ and OR is the dominant sintering process. At this temperature (973 K< T = 1073K< 1173K) OR could be governed by both surface and gas phase mediated monomers.

Here, we synthesized various Pd-supported materials (i.e., Pd/γ -Al₂O₃, Pd/La-

doped Al_2O_3 , and $Pd/\theta\delta$ - Al_2O_3) and subjected them to aging under oxidative and reductive conditions relevant for TWC operation. The evolution of Pd particle size and dispersion was experimentally monitored with increasing aging time to extract kinetic parameters that were used in computational models describing the sintering kinetics. Although previous sintering models have explored the dependence of sintering parameters on temperature¹¹ and gas phase conditions,²⁶ those models did not incorporate the heterogeneity of support or potential simultaneous sintering mechanisms such as particle migration and coalescence (PMC). Consequently, prior models lack critical physics that needs to explain transient bimodal particle size distributions of Pd on Al_2O_3 . To improve prior models, we include the support heterogeneity in our OR model using different 'patches' to represent varying metal-support interaction strengths while describing the temperature and condition dependency of the sintering kinetic parameters. Finally, we used DFT to provide insights into the plausible structures Pd monomers on the support during sintering, and Pd monomer diffusion rates at different hydroxyl site densities of γ -Al₂O₃. Together, these findings provide fundamental insights on minimizing Pd sintering by changing operating conditions, support properties, and initial Pd particle size and distribution to design materials for TWC application with improved metal utilization for extended lifetimes.

6.2 Experimental Methods

6.2.1 Pd on Al_2O_3 , La-doped Al_2O_3 , and $\theta\delta$ - Al_2O_3 Catalyst Preparation and Aging Treatments Characterization

This section covers the catalyst preparation and aging treatments for Pd supported on γ -Al₂O₃, La-doped Al₂O₃, and $\theta\delta$ -Al₂O₃.

6.2.1.1 Catalyst Preparation using Incipient Wetness Impregnation (IWI)

The IWI method was used with commercially available γ -Al₂O₃ (Sasol Puralox TH 100/150 Lot: B34735 γ -Al₂O₃), La-doped Al₂O₃ (Sasol Puralox TH 100/150 L4 La-doped $\rm Al_2O_3),$ and $\theta\delta\text{-}Al_2O_3$ (Sasol Puralox TH 100/90 High Optical Basicity $\theta\delta$ Phase Al_2O_3) using an aqueous solution of tetraamine Pd nitrate (Tetraamminepalladium(II) nitrate solution, 10 wt.% in H₂O, Sigma Aldrich) to obtain 1 wt.% (± 0.05 wt%) Pd loading. Next, the materials were dried in stagnant air at 358 K overnight. Then, the Pd-supported materials were treated in the following sequence: (i) ramp from 298 K in dry air (Air Zero, Indiana Oxygen) to a temperature between 673 – 1073 K at 0.083 K s⁻¹, hold at desired temperature for 3 h; (ii) ramp from a temperature between 673 – 1073 K to 298 K in dry air (Air Zero, Indiana Oxygen) at 0.083 K s^{-1}, hold at 298 K for 0.5 h; (iii) ramp from 298 K in 5% $\rm H_2/N_2$ (Certified Mixture, Indiana Oxygen) to 473 K at 0.083 K s⁻¹, hold at 473 K for 0.5 h then continue ramping to 573 K at 0.083 K s⁻¹, hold at 573 K for 0.5 h; (iv) ramp from 573K in 5% $\rm H_2/N_2$ (Certified Mixture, Indiana Oxygen) to 298 K at 0.083 K $\rm s^{-1},$ hold at 298 K for 0.5 h; (v) purge with N_2 (UHP, 99.999%, Indiana Oxygen) at 298 K for 0.5 h.

6.2.1.2 Catalyst Preparation using Colloidal Pd Nanoparticle Solutions

The syntheses of colloidal Pd nanoparticle solutions were performed using protocols reported by Goodman et al.²⁷ Palladium (II) acetylacetonate (Pd(acac)2, 35% Pd, Acros Organics), 1-dodecene (DDE, 93-95%, Acros Organics), 1-octadecene (ODE, 90%, Acros Organics), 1-tetradecene (TDE, 94%, Alfa Aesar), oleylamine (OAm, technical grade, 70%, Sigma Aldrich), oleic acid (OAc, 90%, Sigma Aldrich), trioctylphosphine (TOP, 97%, Sigma Aldrich), hexanes (99.5%, Fisher Scientific), ethanol (99.5%, Fisher Scientific), isopropanol (99.5%, Fisher Scientific), and methanol (99.8%, Fisher Scientific) were used without further purification.

6.2.1.3 Aging Treatment in O₂

For the aging treatment in O_2 , the Pd-supported samples were treated in following cycle: (i) ramp up from 298 K in 10% O_2 , 10% H_2O , balance N_2 by blending a dry air (Air Zero, Indiana Oxygen) with N_2 (UHP, 99.999%, Indiana Oxygen) that flows through a line connected to a syringe pump (Legato 100 Single Syringe Infuse Only Syringe Pump, KD Scientific) introducing water to 1073 K at 0.083 K s⁻¹, hold at temperature for different time intervals, 2, 6, 12, 24, and 48 h; (ii) ramp from 1073 K to 298 K in 10% O_2 , 10% H_2O , balance N_2 at 0.083 K s⁻¹, hold at 298 K for 0.5 h; (iii) purge with N_2 (UHP, 99.999%, Indiana Oxygen) at 298 K for 0.5 h.

6.2.1.4 Aging Treatment in H₂

For the aging treatment in H_2 , the Pd-supported samples were treated in following cycle: (i) ramp up from 298 K in 2% H_2 , 10% H_2O , balance N_2 by blending a 5% H_2/N_2 (Certified Mixture, Indiana Oxygen) with N_2 (UHP, 99.999%, Indiana Oxygen) that flows through a line connected to a syringe pump (Legato 100 Single Syringe Infuse Only Syringe Pump, KD Scientific) introducing water to 1073 K at 0.083 K s⁻¹, hold at temperature for different time intervals, 2, 6, 12, 24, and 48 h; (ii) ramp from 1073 K to 298 K in 2% H₂, 10% H₂O, balance N₂ at 0.083 K s⁻¹, hold at 298 K for 0.5 h; (iii) purge with N₂ (UHP, 99.999%, Indiana Oxygen) at 298 K for 0.5 h.

6.2.2 Pd on Al_2O_3 , La-doped Al_2O_3 , and $\theta\delta$ - Al_2O_3 Catalyst Characterization

Below we describe details of elemental composition of Pd by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Thermo Scientific iCAP 7000 Plus Series ICP-OES and palladium surface area measurements by O_2 chemisorption using a Micromeritics ASAP 2020 Plus Chemisorption unit for fresh and aged Pd supported on γ -Al₂O₃, La-doped Al₂O₃, and $\theta\delta$ -Al₂O₃ materials.

Pd-supported materials (typically 0.02-0.03 g) were dissolved in 2.0 g of HF (48wt%, Alfa Aesar) for 48 h and 2.5 g of aqua regia, prepared from a 3:1 mass ratio of 37 wt.% HCl (37 wt%, Macron) and HNO₃ (70 wt %, Sigma-Aldrich), for 48 h and then further diluted with 50 g of deionized water. These digested samples are analyzed by ICP-OES analysis, and the elemental composition of Pd were determined from calibration curves generated by elemental analysis standard solutions. Also, the elemental composition of Pd-supported was further validated by calculating the amount of Pd (Pd wt%) added during the IWI with the aqueous of tetraamine Pd nitrate solution.

Then, the dispersion of the Pd-supported samples was measured using H_2 -O₂ chemisorption. The basic procedure consisted of samples (0.25 g) were dehydration

in He (UHP, 99.999%, Indiana Oxygen) at 373 K for 0.5 h, then a leak test was performed to confirm that leak rates were below the threshold of <600 μ mHg h⁻¹ (recommended by Micromeritics). Samples were then treated using Pd-membranepurified H₂ (UHP, 99.999%, Indiana Oxygen) at 673 K for 0.5 h, and an evacuation for 0.5 h at the same temperature before cooling to the analysis temperature 308 K in O₂ (UHP, 99.98%, Matheson) from 10–300 mmHg. A stoichiometry of one O per surface Pd was assumed to estimate the Pd surface dispersion.²⁸

Transmission electron microscopy (TEM) images were acquired using an FEI Tecnai T20 TEM equipped with a 200 kV LaB6 filament. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected using the FEI Talos F200X S/TEM equipped with a 200 kV X-FEG field-emission source. Colloidal solutions for TEM were prepared by drop casting onto a carboncoated Cu grid. The Pd-supported materials (\approx 5 mg) were sonicated in 1 mL ethanol for 15 min prior to drop casting onto Cu grids. Samples were imaged under vacuum (c.a. 10 µPa).

6.2.3 Measurement of Ethylene Hydrogenation Kinetics under Differential Conditions

Ethylene hydrogenation catalytic experiments were carried out in a plug-flow reactor at 258 K. These sub-ambient temperatures were achieved by cooling with liquid nitrogen flow through a cooper heat exchanging coil wrapped around a 316 stainless steel reactor and controlled by a switching valve. Experiments were conducted over a range of ethylene (99.95%, Matheson) partial pressures ranging from 20 – 200 kPa and a range of hydrogen (99.999%, UHP, Indiana Oxygen) partial pressures ranging from 20 – 200 kPa with balance He (99.999Methane (99.995%, Matheson) was co-fed as an internal standard for quantification using gas chromatography (GC) analysis. Gas-phase products were analyzed using an Agilent Technologies 6890N Gas Chromatograph equipped with a flame ionization detector. Prior to ethylene hydrogenation reactions, catalysts were pretreated in flowing H_2 and heating at a rate of 5 K min⁻¹ up to 473 K and holding for 0.5 h before decreasing the temperature to the reaction temperature, 258 K.

6.2.4 Binding energy calculations for Pd anchoring sites on Al_2O_3

DFT calculations were performed to estimate the binding energy of Pd in different anchoring locations. An ensemble of γ -Al₂O₃ surfaces was taken from a previous study,²⁹ including hydroxylated, non-hydroxylated, and surfaces with defects. Then, Pd was placed in different symmetry unique surface locations to examine the binding energy differences among different anchoring sites. We optimized all the initial structures using DFT calculations carried out using the Vienna Ab Initio Simulation Package³⁰ (version 5.4.4). The projector-augmented wave^{30,31} method of core valence interactions and a plane wave cutoff energy of 400 eV was used. The generalized gradient approximation functional of Perdew–Burke–Ernzerhof (PBE)³² was used to describe the exchange-correlation potential with the Becke-Johnson damping method (D3(BJ)vdw)^{33,34} included for dispersion corrections. The electronic energies were converged to 10⁻⁶eV and atomic forces to less than 0.03 eV Å⁻¹.

Subsequently, Pd diffusion barriers were computed between one site to a neighboring site using ab initio metadynamics performed in VASP 6.1.0 for anchoring sites

that are either thermodynamically preferable or statistically present in large quantities.

6.2.5 Simulations for sintering rate predictions

To model the kinetics of Pd sintering, we used a previously developed meanfield OR model^{35,36} described in Appendix-B. This OR sintering model is applicable for both surface or gas phase mediated OR. The system of ODEs was integrated with SciPy *solve_ivp* package and averaged 100 independent simulations to converge. Then, kinetic parameters were regressed to the measured average particle size from chemisorption using a grid search first and then using L-BFGS-B algorithm as implemented in the Python Scipy package³⁷ to minimize the model error. Subsequently, these regressed kinetic parameters were validated by extrapolating to longer sintering times and comparing the model predictions for different particle size distributions to results from TEM. Finally, correlations were developed between the regressed kinetic parameters and computed quantities, such as Pd binding energies and diffusion barriers on different alumina surfaces, and Pd particle surface energies under different gas environments.

6.3 Results and Discussion

Pd was supported on Al_2O_3 using incipient wetness impregnation (IWI) and solution-phase colloidal synthesis methods²⁷ to isolate the effects of Pd particle size and distribution on the sintering rates. The Pd/Al₂O₃ samples were characterized using O₂ chemisorption and transmission electron microscopy (TEM), resulting in similar average Pd particles with differing Pd particle size distributions for the different metal deposition methods. Furthermore, IWI resulted in log normal distribution (LND) of Pd particle sizes, while colloidal synthesis methods led to a normal distribution (ND) of Pd particle sizes (Figure B.3, Figure B.4). Samples are referred to as Pd-X-ND or LND/Al_2O_3 , where X is the average particle diameter (in nm) estimated from chemisorption on the as-deposited colloidal syntheses and after post-deposition treatments for IWI syntheses, where the prefix ND denotes normal distribution of particle sizes, and LND denotes a log-normal distribution of particle sizes present before aging treatments, as determined by TEM.



Figure 6.1: Comparison of average Pd particle sizes on Pd-2.3-LND/Al₂O₃ after oxidative (blue, 10 kPa O₂, 10 kPa H₂O, balance N₂) and reductive (red, 2 kPa H₂, 10 kPa H₂O, balance N₂) aging treatments at 1073 K at 0.083 K s⁻¹ holding for 2, 6, 12, and 24 h quantified by O₂ chemisorption.

To capture the wide range of operating conditions TWCs experience during vehicle operations⁷ (e.g., O_2 and/or H_2 gas environments in the presence of H_2O), the Pd-2.3-LND/Al₂O₃ was treated to high temperatures (1073 K) in flowing air (10 kPa O_2 , 10 kPa H_2O , balance N_2) or hydrogen (2 kPa H_2 , 10 kPa H_2O balance N_2) and the extent Pd particle sintering in those gas environments was measured as a function of treatment time using O_2 chemisorption and TEM. Under the O_2 environment, the average Pd particle size increased with treatment time, reaching a pseudo steady state average Pd particle sizes of 6.0 nm determined by O_2 chemisorption (Figure 6.1), consistent with previous reports observing a decrease in Pd dispersion as a function of treatment time.¹⁴ Similarly, for the reductive aging conditions, the average Pd particle size increased with treatment time but reached a significantly higher pseudo steady state average Pd particle size of 12.8 nm, as measured by chemisorption. These results are consistent with the observation of Chen et al. from STEM and CO oxidation conversion measurements that treatments containing \mathbf{H}_2 lead to more severe sintering than treatments without H_2 .¹² Therefore, when Pd particles with the same initial particle size distributions are treated to 1073 K under 2 $\rm kPaH_2$ and 10 $\rm kPa$ $\rm H_2O$ compared to 10 kPa $\rm O_2$ and 10 kPa $\rm H_2O,$ the treatment under $\rm H_2$ is expected to have higher sintering rates because: (1) metallic Pd particles have higher surface energy (γ) per Pd atom than PdO,³⁸ and according to other previous kinetic models higher surface energies should result in faster sintering rates, 13 (2) H atoms form Pd-H species on the surface of Pd particles and weaken the Pd metal γ -Al₂O₃ support interaction which may lower the activation energy to form Pd monomers for sintering, (3) weakening of the bond strength of Pd particles with the support in the presence of H_2 , which facilitate particle migration and coalescence (similar behavior is reported in the presence of the hydrocarbons).³⁹

To isolate the effects of Pd particle size and support properties on the extent of Pd sintering after oxidative and reductive aging, Pd was supported on La-doped



Figure 6.2: Comparison of average Pd particle sizes on Pd-2.9-LND/La doped-Al₂O₃ after oxidative (light blue, 10 kPa O₂, 10 kPa H₂O, balance N₂) and reductive (magenta, 2 kPa H₂, 10 kPa H₂O, balance N₂) aging treatments at 1073 K at 0.083 K s⁻¹ holding for 2, 6, 12, and 24 h quantified by O₂ chemisorption.

 Al_2O_3 and $\theta\delta$ - Al_2O_3 with approximately the same initial average particle size as the Pd-2.3-LND/ Al_2O_3 . Similar to Pd-2.3-LND/ Al_2O_3 , the Pd-2.9-LND/La-doped Al_2O_3 and Pd-2.7-LND/ $\theta\delta$ - Al_2O_3 were aged under oxidative (10 kPa O_2, 10 kPa H_2O , balance N₂) and reductive (2 kPa H₂, 10 kPa H₂O, balance N₂) conditions as a function of treatment time. For both the Pd-2.9-LND/La-doped Al_2O_3 and Pd-2.7- $LND/\theta\delta$ - Al_2O_3 , at a given treatment time the aging treatments in H₂ resulted in a greater extent of sintering than when the aging treatment was done in O₂ as shown in Figure 6.2. Previous reports show doping Al_2O_3 supports with lanthanum⁴⁰⁻⁴² or increasing the initial thermal treatments in air of the Al_2O_3 support to form preferred structural intergrowths, θ -phase,^{25,43,44} stabilize the support at high temperatures (>1073 K) and prevent the transition to the less favorable α -Al₂O₃. Furthermore, Smith et al.⁴¹ show the transition from γ -Al₂O₃ to α -Al₂O₃ happens at around 1223 K in air, and adding La to γ -Al₂O₃ increases this transition temperature by 100 K. Also, Stumpf et al.⁴⁵ studied the thermal decompositions of pure alumina hydrates and showed with X-ray diffraction (XRD) the crystallite structure changed as the temperature was increased to 1473 K in dry air resulting in more stable forms of Al₂O₃(thermodynamically favorable structures) further supported and developed to progress from boehmite to γ -Al₂O₃ to δ -Al₂O₃ to θ -Al₂O₃ to α -Al₂O₃.⁴⁶⁻⁴⁸ Our aging experiments for Pd on different Al₂O₃ supports were performed at 800 K, so the supports should be thermally stable, and unless La or the $\theta\delta$ -phase change the extent of sintering when compared to Al₂O₃, sintering rates should be the same. Indeed, our data in Figure 6.2 show that Pd sintering is unaffected by the alumina support type. Therefore, the support properties of La-doped Al₂O₃ and $\theta\delta$ -Al₂O₃ had no effect on the extent of sintering when compared to γ -Al₂O₃ at 1073 K) signifying the doped La or $\theta\delta$ -phase did not have an impact on the Pd sintering rate.

To understand the effect of the initial particle size distribution on sintering rates, we studied the Pd-2.4ND-Al₂O₃ sample, where the initial particle size distribution is normally distributed (Figure B.4). Figure 6.3 shows that during reductive aging, the average particle size monotonically increases slower than in Pd-2.3LND-Al₂O₃ from 2.4 nm to 5.5 nm during the initial 6 h of aging and increases minimally after. The lower average Pd particle sizes observed for Pd-2.4-ND/Al₂O₃ than Pd-2.3-LND/Al₂O₃ after reductive aging treatments at the same treatment time suggest that narrower particle size distributions (prepared with colloidal synthesis) have slower sintering rates than broader particle size for both distributions. This is expected because the



Figure 6.3: Comparison of average Pd particle sizes on Pd-2.4-ND/Al₂O₃ after oxidative (blue, 10 kPa O₂, 10 kPa H₂O, balance N₂) and reductive (red, 2 kPa H₂, 10 kPa H₂O, balance N₂) aging treatments at 1073 K at 0.083 K s⁻¹ holding for 2, 6, 12, and 24 h quantified by O₂ chemisorption.

driving force (per atom free energy in particles) for Ostwald ripening in the narrower particle size distributions is lower than for broader distributions, as shown in previous reports.^{13,20} However, the average particle size during oxidative aging increases at a higher rate in Pd-2.4ND-Al₂O₃ than in Pd-2.3LND-Al₂O₃ during 0-6 h of aging time and then slightly decreased from 10 nm to 7.5 nm during 12 h 24 h interval. Decreasing particle size is not observed for the Pd-2.3LND-Al₂O₃ sample and is atypical for sintering studies where the average size of the particles always grows with time.¹⁴ Moreover, under oxidative conditions, the average particle size grows faster than under reductive aging conditions for the Pd-2.4ND-Al₂O₃. Further, the size distribution analysis using TEM (Figure 6.4) shows that the PSDs became bimodal for both



Pd-2.4ND-Al₂O₃ and Pd-2.3LND-Al₂O₃ after 12 h of oxidative aging, suggesting oxidative and reductive sintering follow different mechanisms.

Figure 6.4: Particle size distributions from TEM for Pd-2.3-LND/Al₂O₃ and Pd-2.4-ND/Al₂O₃ samples under oxidative (10 kPa O₂, 10 kPa H₂O, balance N₂) and reductive (2 kPa H₂, 10 kPa H₂O, balance N₂) aging treatments at 1073 K at 0.083 K s⁻¹ holding for 0, 6 and 12 h. The first column in each raw (0 h) corresponds to the initial particle size distribution. The total number of particles imaged (N), arithmatic average ($\mu_{\rm ND}$), standard deviation($\sigma_{\rm ND}$) and log-normal parameters ($\mu_{\rm LND}, \sigma_{\rm LND}$) of each distribution are shown in the upper right corner of each distribution with the corresponding normal (solid black) and log-normal (dashed line) distributions.

To understand how a bimodal distribution evolves from a unimodal initial size distribution and the differences in sintering rates observed for $Pd-2.4ND-Al_2O_3$ and

 $Pd-2.3LND-Al_2O_3$ samples, we developed a sintering kinetic model using OR theory. To explain the bimodal size evolution, we used two separate support regions with different adhesion strengths, as proposed in a previous study.⁴⁹ Our DFT calculations (Table B.1) show that the Pd monomer binding energy on γ -Al₂O₃ surfaces and interfaces varies significantly $(-200 \text{ to } -60 \text{ kJ mol}^{-1})$ with the local atomic environment of the site. Although these DFT calculations are done with a single Pd atom for simplicity and factors such as gas environment,⁵⁰ degree of surface hydroxylation,⁵¹ and Pd particle shape and size 52-54 can change those binding energies, we expect the adhesion energy between Pd particles and Al_2O_3 support to follow the same qualitative trend. These variations in Pd binding energies to different $\mathrm{Al}_2\mathrm{O}_3$ surfaces and grain boundaries further justify using two (or more) kinetic parameter sets to represent different adhesion strengths between the support and Pd particles. As a first approximation, we considered these two regions as not coupled (Section B.1.6.1), meaning Pd monomers do not travel from one region to another. Next, we regressed kinetic parameters for $Pd-2.3LND-Al_2O_3$ against the average particle size measured from O_2 chemisorption. Regressed values are shown in Table 6.1 top two rows and model predictions using those parameters are shown in Figure 6.5a. Regressed parameters reveal that the slower sintering rate under oxidative conditions observed for the LND sample is mainly governed by the lower L_1 value. This is expected as L_1 is directly proportional to the surface energy of the particles (equation B.20), and oxidation lowers the surface energy of Pd.⁵⁵

Next, assuming neither the sintering mechanism nor properties of the support and Pd particles change, we should be able to predict the sintering under relevant gas conditions using the same kinetic parameters extracted from Pd-2.3LND-Al₂O₃ with the initial particle size distribution corresponding to Pd-2.4ND-Al₂O₃. Our pre-

	Region -1 (fast)		Region-2 $(slow)$	
	$K_1 \; (\mathrm{m}^{-2} \mathrm{s}^{-1})$	$L_1 (\mathrm{nm})$	$K_2 \ ({\rm m}^{-2}{\rm s}^{-1})$	$L_2 (\mathrm{nm})$
LND-oxidative	2.0×10^{-2}	1.4	2.1×10^{-2}	5.0×10^{-2}
LND-reductive	1.5×10^{0}	1.8	2.8×10^{-2}	9.0×10^{-1}
ND-oxidative	4.9×10^{-2}	4.1	8.0×10^{-2}	1.0×10^{-2}
ND-reductive	2.0×10^{-2}	1.4	2.0×10^{-2}	$5.0{\times}10^{-2}$

Table 6.1: Regressed kinetic parameters for two region OR models, with the LND sample consisting of 0.7 of Pd in the fast region and ND samples consisting of 0.98 of Pd in the fast region.



Figure 6.5: Regressed OR model predictions (solid lines) of the average Pd particle sizes for oxidative (blue, 10 kPa O_2 , 10 kPa H_2O , balance N_2) and reductive (red, 2 kPa H_2 , 10 kPa H_2O , balance N_2) aging treatments for (a) Pd-2.3-LND/Al₂O₃, and (b) Pd-2.4-ND/Al₂O₃. The markers are the average particle sizes at 0, 2, 6, 12, and 24 h quantified by O_2 chemisorption.

vious work¹³ shows the validity of this method for Pd supported on CHA zeolite. However, for the $PdAl_2O_3$ system, this is not true, as shown in Figure *B.6*. In fact, for these kinetic parameters, reductive sintering was higher than oxidative and therefore, we hypothesized that one reason for this could be that the relative ratios of the two support regions are different for the two samples. The polarities of solvents used are significantly different for the IWI and colloidal synthesis, therefore, the solvated Pd nanoparticle precursors may deposit on these two hypothetical regions disproportionately. To test this hypothesis, we regressed the fraction (f) of Pd particles in the fast region, (correspond to the larger average size mode at t=12 h), while keeping the same kinetic parameters. However, no value of f (0 < f < 1) reproduced the higher initial sintering rates in oxidative aging for the ND sample observed in experiments. This observation suggests that the kinetic parameters could differ for the ND and LND samples, potentially due to the presence of residual capping agents in ND sample and differences in Pd particle morphology.

Therefore, to find a parameter set that can explain our experimental sintering data for the $Pd-2.4ND-Al_2O_3$ sample, we independently regressed the experimental sintering data (size vs. time) (Figure 6.5b). The regression kinetic parameters are shown in Table 6.1 bottom rows and the fraction of Pd in the fast kinetic region is 0.98 for colloidally synthesized Pd, which is significantly higher than the fraction of Pd in the fast region observed for IWI synthesized Pd (f = 0.7). These differences suggests that the colloidal synthesis drives Pd particles to different regions of the support than IWI. This is unsurprising as the capping agents and solvents used in colloidal synthesis might direct particles to different regions of the support because the solvent can experience the same adhesion energy difference that Pd particles experience. Further, the kinetic parameters under reductive aging for $\mathrm{Pd}\text{-}2.4\mathrm{ND}\text{-}\mathrm{Al}_2\mathrm{O}_3$ sample are closer to the parameters regressed for oxidative aging of the Pd-2.3 LND- Al_2O_3 sample, indicating that the slow sintering of Pd-2.4ND- Al_2O_3 under reductive aging is attributed to different material properties. One reason could be the presence of P agents in the system increasing the free energy of monomer generation (lower parameters K_1 and K_2) and/or lower the surface energies of particles (parameter L_1

and L_2). Further experiments are required to test this hypothesis. Another reason for these differences in kinetic parameters could be the multiplicity of the parameter optimization solution that might be overlooked during the grid search; a comprehensive global optimization protocol is required to identify other combinations of the kinetic parameters that give an acceptable accuracy for fitting while constraining the parameters to be the same for both LND and ND systems.

Despite the differences in kinetic parameters that we do not fully understand yet, the sintering simulations produces bimodal size distributions over time (Figure 6.6) as expected from the model's governing equations. However, our simulations (using the regressed parameters) show lower mode separation than the experimental size distributions (Figure 6.5). Moreover, in the simulations, both oxidatively and reductively aged samples show a bimodal evolution over time, whereas in experiments, only oxidative aging shows clear bimodal size distribution evolution. However, Chen et al.⁵⁶ observed bimodal size distributions evolving from uni-modal initial size distributions as Pd particles supported on Al_2O_3 sinter under 101 kPa H_2 environment for 1, 4 and 20 h at 1073 K, qualitatively consistent with our simulated particle size distributions. At larger particle sizes, especially under high temperature oxidative conditions where hydroxyl group coverage is low, Pd particles are likely to wet the alumina surface forming flat disk-like particles,^{51,57} resulting in underestimated particle sizes from O₂ chemisorption (e.g. 6.0 vs 39.5 nm), and leading to other modes of sintering, such as coalescence.⁵⁸ Nevertheless, our OR simulations qualitatively capture the bimodal size distributions while quantitatively accurately capturing the variations of average particle size (from O_2 chemisorption) vs time.





Figure 6.6: Particle size distributions from simulations for Pd-2.3-LND/Al₂O₃ and Pd-2.4-ND/Al₂O₃ holding for 0, 6 and 12 h under oxidative (10 kPa O₂, 10 kPa H₂O, balance N₂) and reductive (2 kPa H₂, 10 kPa H₂O, balance N₂) aging treatments at 1073 K. The first column in each raw (0 h) corresponds to the initial particle size distribution, initiated to be consistent with TEM. The total number of particles (N), arithmatic average ($\mu_{\rm ND}$), standard deviation($\sigma_{\rm ND}$) and log-normal parameters ($\mu_{\rm LND}$, $\sigma_{\rm LND}$) of each distribution are shown in the upper right corner of each panel with the corresponding normal (solid black) and log-normal (dashed line) distributions.

6.4 Conclusions

We combined precise catalyst synthesis methods, quantitative surface metal characterization techniques, and computational sintering models to understand the influence of operating condition, support properties, initial Pd particle size, and initial Pd particle size distribution on Pd sintering rates and mechanisms. To quantitatively access the sintering rates and their dependencies on initial Pd particle size and initial Pd particle size distribution, a suite of supported Pd materials were prepared using IWI of Pd to form log-normal Pd particle size distributions and deposition of colloidal Pd nanoparticle suspensions to form normal Pd particle size distributions. Regardless of the gas environment for aging, the normal distribution of Pd supported materials resulted in a lower extent of sintering than log-normal distribution of Pd particles at fixed conditions and treatment times. Also, the oxidative and reductive gas environments for aging change Pd sintering rates significantly and result in particle size distributions consistent with dispersion measured with chemisorption. Pseudo steady state sintering is achieved for the average Pd particle sizes at a 6 to 24 h time scale. However, Pd particles may still be sintering at slow rates as suggested by previous studies.¹⁴ Furthermore, the sintering studies of Pd supported on various Al_2O_3 showed that the sintering rates are insensitive to the Al_2O_3 support type. Finally, our regressed OR kinetic model recovered the transient bimodal evolution of particle size distributions. The model also suggests that the relative ratios of Pd in the two regions of the support for different synthesis methods are significantly different (70% Pd in the fast region for IWI synthesis and 98% Pd in the fast region for colloidal synthesis) and could provide insights into the parameters relevant for stabilizing Pd particles against sintering. Further, the kinetic parameters are different for the two synthesis methods, suggesting that the two synthesis methods give different energy barriers for monomer generation or particle morphologies that can affect those parameters. These experimental and computational findings give insights into the conditions and materials properties controlling the Pd sintering and redispersion processes, allowing for synthetic strategies to minimize Pd sintering to be able to design materials for catalytic applications with improved metal utilization and extended lifetimes.

6.5 Future Work

6.5.1 Strategies to Understand Properties Influencing Pd Sintering Kinetics

The data collected thus far partially addresses how the initial Pd particle size and gas environment affect the sintering kinetics on the same support. Kang et al.¹¹ and Lardinois et al.¹³ have experimentally shown that the Pd particles with the largest initial particle diameters show lower sintering rates than smaller Pd particles. Therefore, our immediate future work will be to age Pd/Al_2O_3 materials with different initial particle sizes (2–10 nm) to corroborate or refute larger initial Pd particle sizes supported on Al_2O_3 to have lower sintering rates. Then, the Pd/Al_2O_3 materials with different initial particle sizes will be aged under oxidative (10 kPa O_2 , 10 kPa H_2O , balance N_2) and reductive conditions (2 kPa H_2 , 10 kPa H_2O , balance N2) to determine how gas environments affect the sintering kinetics. This future work will give insight into the effect of initial particle size and gas environment on the sintering kinetics of $\rm Pd/Al_2O_3$ materials. Also, Cao et al. reported that Pd supported on γ -Al₂O₃ and Ce_{0.5}Zr_{0.5}O₂ (CZ) had different extents of sintering when treated under the same gas environment and time.¹⁹ This was explained due to strong metal support interactions (i.e., strong Pd-O-Ce bonds) on the Pd/CZ material that is absent on the Pd/γ -Al₂O₃. Furthermore, our Pd sintering data for Pd-2.3-LND/Al₂O₃ and $Pd-2.4-ND/Al_2O_3$ and regressed kinetic parameters show different degree of support heterogeneity. Supported palladium particles prepared by IWI and colloidal synthesis may contain Pd in different regions of the support due to polarity differences in solvents used and capping agents used in colloidal synthesis may influence the sintering rates. Therefore, future work will be to support Pd using IWI on various Al_2O_3 supports using non-polar solvents such as C_6H_6 with the $Pd(acac)_2$ precursor used in colloidal synthesis. This will allow us to understand whether the polarity difference in solvents play a key role determining the heterogeneity of metal support interactions invoked in our simulations.

6.5.2 Structure Insensitive Reaction to Quantify the Surface Pd after Aging Treatments

This future work will focus on understanding the amount of surface Pd remaining after aging under oxidative and reductive conditions and how Pd particle size changes after being hydrothermally treated as a function of time. Chemisorption and TEM are commonly used to access and quantify the metal dispersion of a metal-supported sample of arbitrary origin. However, there are complications when comparing the Pd particle size between chemisorption and TEM because chemisorption is a bulkaverage technique while TEM is a localized technique. Hence, the proposed technique to help resolve any discrepancies between the Pd particle sizes after aging treatments is measuring ethylene hydrogenation kinetics because this reaction has been shown to be a structure-insensitive reaction, and therefore, every exposed metal atom has the same rate independent of the particle size or support type.⁵⁹⁻⁶¹ First, the kinetic regimes (i.e., range of ethylene and hydrogen orders) for two model Pd supported materials of different initial Pd particle sizes (2 - 10 nm) will be found to determine the ethylene and hydrogen pressures leading to the same kinetic regime for materials regardless of Pd particle size. Then, a trend in rate and/or rate constant and surface Pd per total Pd will be developed for that model Pd supported materials to be able to extract the amount of surface Pd per total Pd when the ethylene hydrogenation rate is measured on Pd supported materials of arbitrary origin. These experiments should be run at the same kinetic regime (i.e., hydrogen and ethylene pressures leading to the same reactant orders), to compare the rates and/or rate constants for each of supported Pd materials to extract the amount of surface Pd on the material after a new synthesis or aging treatment. Furthermore, ethylene hydrogenation reaction offers a method to quantify the amount of surface Pd after aging treatments based on the intrinsic properties of the metal sites. Therefore, this future work will be used to extract rates and/or rate constants to determine the number of surface Pd sites after aging under oxidative and reductive conditions to not only help understand the sintering kinetics but also to corroborate the amount of surface Pd from chemisorption and TEM characterization techniques.

6.5.3 Investigate coupled heterogeneous regions with the OR model.

All simulations discussed above are from the scenario of uncoupled support regions. However, high mobility of monomers can cause two support regions to be able to exchange monomers and our derived governing equaitons (B.23-B.25) will capture those processes. This model with single monomer pool may have different parameter values and particle size evolution patterns over time. Therefore, we aim to explore this system and then the kinetic parameters and the quality of regression can be compared to find the best model for Pd/Al_2O_3 system under oxidative and reductive aging conditions.

6.5.4 Global search of sintering model parameters

Currently we used a grid search to regress parameters of our mean field model to the experimental sintering data (size vs time) and the simulations discussed above used the best fit parameters for each gas condition and support. However, there will be more than one parameter set that can give an acceptable model error. In future, we will explore multiple kinetic parameter sets to see whether more than one combination of parameters will give a satisfactory fit and then rule out parameter sets based on the physical properties of Al_2O_3 support and Pd particles to retain physically reasonable parameter sets. This will allow us to interpret the parameters and draw conclusions based on their variations with the aging gas environment and support properties.

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Chapter 7

Contributions to Other Research Projects

I have been working with several Chemical Engineering undergraduate students, group members, and groups from other institutions to work on different research projects. I worked with my fellow coworker, Dr. Keka Mandal, to systematically generate a library of binuclear Cu structures for CHA in one of her primary projects: (Mandal, K.; Rani, P.; Chen, Y. R.; Wijerathne, A.; Nam, K.; Kiani, D. A.; Daya, R.; Epling, W. S.; and Paolucci, C. Impact of Sulfur Exposure on High-Temperature Cu Speciation in SSZ–13 Zeolites, *In Preparation*). To investigate the effect of high-temperature sulfur exposure on dimeric Cu species in CHA zeolites, we use a combined computational and experimental approach. Keka performed thermodynamic analysis using DFT calculations of the structures I generated, and the Epling lab at UVA used CO titration and UV-vis spectroscopy to characterize the Cu species in the system and measured SCR rates to interrogate the influence of each species on the SCR performance. The manuscript encompassing this work is being prepared.

I worked with Isabelle Deadman, a UVA undergraduate (2021–2023), to investigate the reaction energies of NH_3 solvated Cu complexes in Cu-SAPO34 and Cu-SSZ-13, relevant to the conditions of SCR. We used enhanced sampling using metadynamics for exploring the minima of the system and estimation of the reaction free energy. This work has not been published due to time constraints, but after graduation, I plan to work on the data we collected and complete the analysis.

Currently, I am working with another UVA undergraduate, Amish Madhav, and Tala Mon, a PhD student in Prof. Eleni Kyriakidou's lab at the University of Buffalo, to investigate the Pd-PdO interconversion and Pd²⁺ cation speciation in BEA zeolites. Our experimental collaborators use CH_4 oxidation as a probe reaction to estimate the fraction of PdOx species in the system while we computationally assess the formation energies of these species using DFT. Moreover, I helped Amish calculate the vibrational frequencies for CO and NO bound cationic species (e.g., Z_2Pd -CO, ZPdOH-CO). Those computed frequencies associated with each structure and the experimental spectra collected by UB collaborators will allow us to identify dominant species during the reaction. As a coauthor, I am contributing to the manuscript writing of this work (Mon, T.; Concolino, J.; Madhav, A.; Wijerathne, A; Chen, J.; Paolucci, C.; and Kyriakidou, E. A. Pd Speciation of Pd/BEA and Pd/CHA Catalysts when Exposed to Ambient Moisture, *In Preparation*)
Chapter 8

Final Conclusions and Outlook for the Future

In the work reported in this dissertation, we used computational modeling tools such DFT, thermodynamic analysis to estimate the cation speciation in zeolites and kinetic modeling of thermal and chemical deactivation of supported metal catalysts. By combining available open source software packages and theory, we developed new techniques such as high-throughput structure sampling with a sequential use of classical force field and a machine learning potential trained for Cu exchanged zeolites.¹

In Chapter 2, we found that the Al distribution is critical for biasing dimeric Cu over monomeric Cu. Our study focused on relatively low water pressure conditions due relative simplicity of the system. However, in some of practical applications such as selective catalytic reduction, molecules such as NH_3 and H_2O present in the systems. These molecules can solvate the cations^{2,3} and change the free energies of species. Future studies should focus on the added complexity of H_2O and NH_3 adsorption for these sites.

In Chapter 3 and 4, we model the thermodynamics and kinetics of particle disintegration processes for metals supported on zeolites. These two chapters demonstrate the kinetic model we developed has a wide applicability for explaining redispersion kinetics observed in different systems.⁴ However, in these kinetic simulations, we assumed an irreversible atom trapping reaction and the implications of reversibility of the reaction to the particle redispersion may be explored in the future.

In Chapter 5, our thermodynamic analysis of atom trapping reveals the key limiting factors for atom trapping processes as, (1) the relative density of trapping sites compared to the metal loading of the system and, (2) the atom trapping reaction free energy. However, our approximation of all metal atoms (M) in particles having the same energy breaks down for smaller (< 2 nm) nanoparticles as M atoms in smaller particles are, on average, more under-coordinated and, therefore, higher in energy than those in larger particles. Although, a simple analytical expression cannot be derived for the fraction of single atoms ($X_{trapped}$) without this approximation, the numerical simulation we implemented can be adapted to the size (and/or shape) dependent energies of metal atoms on particles. Currently, we are expanding the numerical simulation including additional free energy driven atom exchange processes such as Ostwald ripening (OR) that could simultaneously occur in a practical systems such as the one described in Chapter 6.

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Appendices

Appendix A

Supporting Information: Thermodynamics and kinetics of interconversion between platinum nanoparticles and cations in zeolites.

A.1 Zeolite Structure Sampling



Figure A.1: DFT computed energy of Z_2Pt structures vs Al-Al distance in CHA for 25 symmetry-distinct 2Al configurations. The nearest neighbor 2Al configurations are color coded as follows: red – 1NN, green – 2 NN, blue – 3NN, orange – 4NN, black – 5 NN. The energies are relative to the lowest energy Z_2Pt structure, 3NN 6MR.



Figure A.2: DFT computed energy of Z_2Pt structures in (a) BEA and (b) TON vs. Al-Al distance for the sampled symmetry-distinct 2 Al configurations. The nearest neighbors are color-coded as follows: green – 2 NN, blue – 3NN, orange – 4NN. The energies are relative to the lowest energy Z_2Pt structure, 3NN 6MR, in both frameworks.

A.2 Thermodynamic Calculations

A.2.1 Configurational entropy for Pt redispersion

Consider a system with Pt particles comprised of $N_{\rm Pt}$ total Pt atoms and $N_{2\rm Al}$ number of Pt exchange sites. Each site can either exchange one Pt atom, forming Z₂Pt or Z₂Pt(H₂O)₂ cationic species, or remain vacant. If the number of ion-exchanged (redispersed) Pt atoms is $n_{\rm Pt}$, then the total number of configurations in the system is given by the product between the number of ways for choosing $n_{\rm Pt}$ Pt atoms out of $N_{\rm Pt}$ total Pt atoms, and from vacancies, choosing $n_{\rm Pt}$ exchange sites out of $N_{2\rm Al}$ to ion exchange. Therefore, the total number of configurations ($\Omega_{\rm config.}$) for ion-exchanged Pt is then given by,

$$\Omega_{\rm config.} = \binom{N_{\rm Pt}}{n_{\rm Pt}} \times \binom{N_{\rm 2Al}}{n_{\rm Pt}}$$
(A.1)

and by definition, the configurational entropy is,

$$S_{\text{config.}} = k_{\text{B}} \ln \left[\binom{N_{\text{Pt}}}{n_{\text{Pt}}} \times \binom{N_{2\text{Al}}}{n_{\text{Pt}}} \right]$$
(A.2)

Assuming the configurational entropy change for particles is negligible compared to the entropy change for cations during the redispersion process, and applying Stirling's approximation to Eq.A.2, results in the following definition for the change in configurational entropy due to ion-exchange:

$$\Delta S_{\text{config.}} = k_{\text{B}} \left[N_{\text{Pt}} \ln \left(N_{\text{Pt}} \right) - \left(N_{\text{Pt}} - n_{\text{Pt}} \right) \ln \left(N_{\text{Pt}} - n_{\text{Pt}} \right) \right]$$

$$k_{\text{B}} \left[N_{\text{2Al}} \ln \left(N_{\text{2Al}} \right) - \left(N_{\text{2Al}} - n_{\text{Pt}} \right) \ln \left(N_{\text{2Al}} - n_{\text{Pt}} \right) - 2n_{\text{Pt}} \ln \left(n_{\text{Pt}} \right) \right]$$
(A.3)



Figure A.3: Pt particle size and temperature-dependent thermodynamic phase diagrams for the conversion of Pt particles to Pt cations and oxides in CHA with the supported particle free-energy model with $\theta = (a) 60^{\circ}$, (b) 90°, and (c) 120°. Each column represents (from left to right) (1) $P_{\rm H_2O} = 0.01$ kPa and $P_{\rm O_2} = 20$ kPa, (2) $P_{\rm H_2O} = 10$ kPa and $P_{\rm O_2} = 20$ kPa, and (3) $P_{\rm H_2} = 10$ kPa.



Figure A.4: Gibbs Free Energy for Pt particle formation as a function of particle size. The orange line, purple dashes, and purple line represent particle energies with $\gamma_{\text{avg,Pt}} = 96.4 \text{ meV}\text{Å}^{-2}$ (Wulff construction-calculated surface energy) for the supported particle free energy model, the unsupported particle free energy model without energy interpolation for small Pt particles (< 2 nm), and unsupported particle free energy model with interpolation, respectively.

	ΔE	ΔG^{form}		
Reaction	$kJ \pmod{Pt}^{-1}$	kJ (mo	$l Pt)^{-1}$	
	, , , , , , , , , , , , , , , , , , ,	550 K	773 K	
ΔG^{form}_{-PtO}				
$Pt_{bulk} + O_2 \xrightarrow{PtO_2} -PtO_2$	-118	-13	22	
$Pt + 4 O = \Delta G_{Pt_3O_4}^{form} \setminus 1 Pt O$	08	20	6	
$1 t_{\text{bulk}} + \frac{1}{3} O_2 \frac{1}{3} 1 t_3 O_4$	-90	-29	-0	
$\mathrm{Pt}_{\mathrm{bulk}} + \mathrm{Z}_{2}\mathrm{H}_{2} \xrightarrow{\Delta\mathrm{G}_{\mathbb{Z}_{2}\mathrm{Pt}}} \mathrm{Z}_{2}\mathrm{Pt} + \mathrm{H}_{2}\mathrm{O}$	67	19	3	
$\Delta G_{\rm Z_2Pt(H_2O)_2}^{form} = D_{\rm C}({\rm U},{\rm O})$				
$Pt_{bulk} + Z_2H_2 + H_2O \xrightarrow{2} Z_2Pt(H_2O)_2$	-109	-1	35	

Table A.1: HSE06-D3(BJ)vdw-calculated formation energies at 0 K (ΔE), and formation free energies (ΔG^{form}) of bulk Pt-metal oxides and CHA Z₂Pt species at 523 K and 773 K, 10 kPa H₂O and 20 kPa O₂.



Figure A.5: Phase diagram, considering vibrational entropies and zero-point energies, of the three most stable ion exchanged Pt/CHA species. The dotted line represents the boundary for the conditions of interest.



Figure A.6: (a) HSE06-computed phase diagram of bulk Pt and Pt-oxides, and their (b) Wulff construction visualizations at select oxygen chemical potentials ($\mu_{\rm O}$).



Figure A.7: CHA size-dependent thermodynamic phase diagram with the unsupported particle free energy model for variations in the average surface energy of Pt $(\gamma_{\text{avg,Pt}})$: (a) 65 meVÅ⁻², (b) 100 meVÅ⁻², and (c) 135 meVÅ⁻². Each column represents (from left to right) (1) $P_{\text{H}_2\text{O}} = 0.01$ kPa and $P_{\text{O}_2} = 20$ kPa, (2) $P_{\text{H}_2\text{O}} = 10$ kPa and $P_{\text{O}_2} = 20$ kPa, and (3) $P_{\text{H}_2} = 4$ kPa.



Figure A.8: CHA size-dependent thermodynamic phase diagram with the supported particle free energy model for variations in the average surface energy of Pt ($\gamma_{\text{avg,Pt}}$): (a) 65 meVÅ⁻², (b) 100 meVÅ⁻², and (c) 135 meVÅ⁻². Each column represents (from left to right) (1) $P_{\text{H}_2\text{O}} = 0.01$ kPa and $P_{\text{O}_2} = 20$ kPa, (2) $P_{\text{H}_2\text{O}} = 10$ kPa and $P_{\text{O}_2} = 20$ kPa, and (3) $P_{\text{H}_2} = 4$ kPa.



Figure A.9: CHA size-dependent thermodynamic phase diagrams with the unsupported particle free energy model for variations in the log-normal standard deviation of the initial particle size distribution ($\sigma_{\rm LN}$): (a) 0.2 nm, (b) 0.3 nm, and (c) 0.4 nm. Each column represents (from left to right) (1) $P_{\rm H_2O} = 0.01$ kPa and $P_{\rm O_2} = 20$ kPa, (2) $P_{\rm H_2O} = 10$ kPa and $P_{\rm O_2} = 20$ kPa, and (3) $P_{\rm H_2} = 4$ kPa.



Figure A.10: CHA size-dependent thermodynamic phase diagrams with the supported particle free energy model for variations in the log-normal standard deviation of the initial particle size distribution ($\sigma_{\rm LN}$): (a) 0.2 nm, (b) 0.3 nm, and (c) 0.4 nm. Each column represents (from left to right) (1) $P_{\rm H_2O} = 0.01$ kPa and $P_{\rm O_2} = 20$ kPa, (2) $P_{\rm H_2O} = 10$ kPa and $P_{\rm O_2} = 20$ kPa, and (3) $P_{\rm H_2} = 4$ kPa.



Figure A.11: Size-dependent thermodynamic phase diagrams with the supported particle free energy model for the conversion of Pt particle to Pt species in (a, b) BEA (NPt/NAl = 0.021, $N_{2Al}/N_{Al} = 0.08$), (c, d) MFI ($N_{Pt}/N_{Al} = 0.036$, $N_{2Al}/N_{Al} = 0.04$), and (e, f) TON ($N_{Pt}/N_{Al} = 0.039$, $N_{2Al}/N_{Al} = 0.05$). The diagrams are calculated at (a, c, e) $P_{H_2O} = 10$ kPa and $P_{O_2} = 20$ kPa and (b, d, f) $P_{H_2} = 10$ kPa.



Figure A.12: Structural change in the CHA 6MR due to Pt ion exchange. The left figure is the DFT-optimized Z_2H_2 structure's 6MR in CHA, and the right is the Z_2Pt structure's 6MR in CHA.

A.3 Kinetic Calculations



Figure A.13: Pt-Pt coordination numbers (CN) at different combinations of the mean (μ) and standard deviation (σ) of (a) unsupported and (b) supported particle sizes, assuming a log-normal distribution.

\bar{x} (nm)	$s_{\bar{x}} \ (\mathrm{nm})$	$\mu_{\rm LN}$ (nm)	$\sigma_{\rm LN} \ ({\rm nm})$	Best fit $\gamma_{\text{avg,Pt}}$ (meVÅ ⁻²)	Best fit $\Delta G_{\text{monomer}}^{form}$ (eV)
0.500	0.311	-0.857	0.572	45	1.35
0.750	0.313	-0.368	0.402	75	1.65
1.00	0.182	-0.0164	0.181	80	1.69

Table A.2: Summary of selected unsupported particle size distributions and temperature-ramp best fit parameters.

$\bar{x} (\mathrm{nm})$	$s_{\bar{x}} \ (\mathrm{nm})$	$\mu_{\rm LN}$ (nm)	$\sigma_{\rm LN} \ ({\rm nm})$	Best fit $(3\gamma_{\text{avg,Pt}} - E_{\text{adh.}})$ (meVÅ^{-2})	$\begin{array}{c} \text{Best fit} \\ \Delta G_{\text{monomer}}^{form} \\ \text{(eV)} \end{array}$
0.500	0.393	-0.934	0.693	110	1.45
0.750	0.468	-0.452	0.574	80	1.30
1.00	0.479	-0.103	0.455	90	1.35
1.25	0.431	0.167	0.335	160	1.69
1.50	0.302	0.386	0.199	210	1.85

Table A.3: Summary of selected supported particle size distributions and temperature-ramp best fit parameters.



Figure A.14: Variation of kinetic model predictions over, 1 (black), 10 (red-brown), 20 (magenta), 50 (green), and 100 (grey) averaged kMC simulations. All kMC simulations are performed with unsupported particle free energy model and simulate the temperature-ramp experiment for $\bar{x} = 0.5$ nm (best-fit parameters: $s_{\bar{x}} = 0.31$ nm, $\gamma_{\text{avg,Pt}} = 45 \text{ meV}\text{Å}^{-2}$, $\Delta G_{\text{monomer}}^{form} = 1.35 \text{ eV}$).



Figure A.15: Impact of $\gamma_{\text{avg,Pt}}$ and $\Delta G_{\text{monomer}}^{form}$ on (a) extent of ion-exchange, (b) Pt-Pt coordination number, and (c-d) particle size distributions of simulations in (a) and (b) as a function of time for the $\bar{x} = 1.25$ nm with supported particle model. All the predictions are for a temperature ramp from 293 to 773 K at 10 K min⁻¹ in 20 kPa O₂. The solid line represents the best fit $(3\gamma_{\text{avg,Pt}} - E_{\text{adh.}} = 160 \text{ meV}\text{Å}^{-2},$ $\Delta G_{\text{monomer}}^{form} = 1.69 \text{ eV}$, while the dashed line represents $3\gamma_{\text{avg,Pt}} - E_{\text{adh.}} = 160 \text{ meV}\text{Å}^{-2},$ $\Delta G_{\text{monomer}}^{form} = 1.6 \text{ eV}$, and the dotted line represents $3\gamma_{\text{avg,Pt}} - E_{\text{adh.}} = 140 \text{ meV}\text{Å}^{-2},$ $\Delta G_{\text{monomer}}^{form} = 1.69 \text{ eV}.$



Figure A.16: Impact of particle size distribution on (a) extent of ion-exchange, (b) Pt-Pt coordination number, and (c-e) particle size distributions as a function of time. (c) Pink, (d) purple, and (e) blue represent the $\bar{x} = 0.5, 0.75, \text{ and } 1.0 \text{ nm}$ unsupported particle distributions, respectively. All the predictions are for a temperature ramp from 293 to 773 K at 10 K min⁻¹ in 20 kPa O₂.



Figure A.17: Impact of particle size distribution on (a) extent of ion-exchange, (b) Pt-Pt coordination number, and (c-g) particle size distributions as a function of time. (c) Yellow, (d) brown, (e) tan, (f) orange, and (g) salmon represent the $\bar{x} =$ 0.5, 0.75, 1.0, 1.25, and 1.5 nm supported particle distributions, respectively. All the predictions are for the temperature ramp experiment.



Figure A.18: Unsupported particle free energy model's predictions of (a) extent of ion-exchange, (b) Pt-Pt coordination number, and (c-e) particle size distributions as a function of time. Simulation results are based on the temperature ramp-fitted $\Delta G_{\text{monomer}}^{form}$ and $\gamma_{\text{avg,Pt}}$ values for $\bar{x} = (c) 0.5$, (d) 0.75, and (e) 1.0 nm, which are depicted by pink, purple, and blue, respectively. The grey points represent experimental data from Moliner et al.¹



Figure A.19: Supported particle free energy model's predictions of (a) extent of ion-exchange, (b) Pt-Pt coordination number, and (c-g) particle size distributions as a function of time. Simulation results are based on the temperature ramp-fitted $\Delta G_{\text{monomer}}^{form}$ and $3\gamma_{\text{avg,Pt}} - E_{\text{adh.}}$ values for $\bar{x} = (c) 0.5$, (d) 0.75, (e) 1.0 nm, (f) 1.25, and (g) 1.5 which are depicted by yellow, brown, tan, orange, and salmon, respectively. The grey points represent experimental data from Moliner et al.¹

					$\Delta G_{\rm mono}^{form}$	ev			
		1.15	1.35	1.45	1.5	1.55	1.6	1.65	1.69
	25	0.0534							
	45		0.00777						
	55			0.0113	0.0340				
$\gamma_{\mathrm{avg,Pt}}$	60			0.0256	0.0159	0.0419			
$(\text{meV}Å^{-2})$	65				0.0320	0.0221	0.0503		
	70					0.0316	0.0278	0.0609	0.107
	75				0.117		0.0362		0.0609
	80						0.0693		0.0403

Table A.4: The sum of squared errors (SSE) between kMC predictions and the extent of ion-exchanged to Pt^{2+} (Moliner et al.¹) during the temperature ramp for the unsupported particle model with $\bar{x} = 0.5$ nm under different $\gamma_{avg,Pt}$ and $\Delta G_{monomer}^{form}$.

				$\Delta G_{\rm monon}^{form}$	$_{\rm ner}({\rm eV})$
		1.55	1.6	1.65	1.69
	65	0.0105	0.0297	0.0797	
$\gamma_{ m avg,Pt}$	70	0.0297	0.00885	0.0280	0.0698
(meVÅ^{-2})	75	0.0797	0.0279	0.00866	0.0247
	80		0.0772	0.0281	0.00932

Table A.5: The sum of squared errors (SSE) between kMC predictions and the extent of ion-exchanged to Pt^{2+} (Moliner et al.¹) during the temperature ramp for the unsupported particle model with $\bar{x} = 0.75$ nm under different $\gamma_{avg,Pt}$ and $\Delta G_{monomer}^{form}$.

			$\Delta G_{\rm mon}^{form}$	$_{\rm comer}^n$ (eV)
		1.65	1.69	1.75
	75	0.126	0.189	0.279
$\gamma_{ m avg,Pt}$	80	0.119	0.110	0.138
(meVÅ^{-2})	85	0.204	0.138	0.115

Table A.6: The sum of squared errors (SSE) between kMC predictions and the extent of ion-exchanged to Pt^{2+} (Moliner et al.¹) during the temperature ramp for the unsupported particle model with $\bar{x} = 1.0$ nm under different $\gamma_{avg,Pt}$ and $\Delta G_{monomer}^{form}$.

					$\Delta G_{\rm mond}^{form}$	$_{\rm omer}^{i}({\rm eV})$		
		1.3	1.45	1.5	1.55	1.6	1.65	1.69
	30	0.0895						
	55		0.0598					
	60		0.0775	0.0781				
$\gamma_{\mathrm{avg,Pt}}$	65		0.0946	0.0881	0.0993	0.106	0.152	
$(\text{meV}Å^{-2})$	70			0.113	0.0963	0.0976	0.122	0.146
	75					0.112		0.135
	80					0.127		0.124

Table A.7: The sum of squared errors (SSE) between kMC predictions and the extent of ion-exchanged to Pt^{2+} (Moliner et al.¹) during the temperature ramp for the supported particle model with $\bar{x} = 0.5$ nm under different $\gamma_{avg,Pt}$ and $\Delta G_{monomer}^{form}$.

					$\Delta G_{\rm mond}^{form}$	$_{\rm omer}^{i}({\rm eV})$		
		1.3	1.45	1.5	1.55	1.6	1.65	1.69
	35	0.0278						
	40	0.0127						
	55		0.0335	0.0665				
$\gamma_{ m avg,Pt}$	60		0.0442	0.0556	0.0700			
$(\text{meV}Å^{-2})$	65			0.0533	0.0584	0.0905	0.142	
	70				0.0616	0.0710		0.122
	75					0.0723		0.103
	80					0.0912		0.0911

Table A.8: The sum of squared errors (SSE) between kMC predictions and the extent of ion-exchanged to Pt^{2+} (Moliner et al.¹) during the temperature ramp for the supported particle model with $\bar{x} = 0.75$ nm under different $\gamma_{avg,Pt}$ and $\Delta G_{monomer}^{form}$.

					$\Delta G_{\rm mond}^{form}$	$_{\rm omer}^{n}({\rm eV})$		
		1.35	1.45	1.5	1.55	1.6	1.65	1.69
	45	0.0095						
	55		0.0104	0.0320				
	60		0.0253	0.0154	0.0350			
$\gamma_{\mathrm{avg,Pt}}$	65			0.0212	0.0212	0.0426	0.0912	
$(\text{meV}^{\text{Å}-2})$	70				0.0346	0.0270	0.0475	0.0859
	75					0.0412		0.0502
	80					0.0719		0.0394

Table A.9: The sum of squared errors (SSE) between kMC predictions and the extent of ion-exchanged to Pt^{2+} (Moliner et al.¹) during the temperature ramp for the supported particle model with $\bar{x} = 1.0$ nm under different $\gamma_{avg,Pt}$ and $\Delta G_{monomer}^{form}$.

			(eV)	
		1.65	1.69	1.75
	75	0.00773	0.0221	0.104
$\gamma_{ m avg,Pt}$	80	0.0235	0.00750	0.0350
(meVÅ^{-2})	85	0.0670	0.0307	0.00943

Table A.10: The sum of squared errors (SSE) between kMC predictions and the extent of ion-exchanged to Pt^{2+} (Moliner et al.¹) during the temperature ramp for the supported particle model with $\bar{x} = 1.25$ nm under different $\gamma_{avg,Pt}$ and $\Delta G_{monomer}^{form}$.

					$\Delta G_{\rm mond}^{form}$	$d_{\rm mer}({\rm eV}))$		
		1.6	1.65	1.69	1.75	1.8	1.85	2.45
	70	0.139		0.276				
	75	0.0730		0.169				
	80	0.0560		0.116				
$\gamma_{ m avg,Pt}$	85	0.149	0.0528	0.0616	0.128			
(meVÅ^{-2})	90	0.192	0.121	0.0515	0.0682			
	95		0.194	0.136	0.0447	0.0656		
	100				0.0948	0.0423	0.0624	
	105					0.0771	0.0397	
	160							0.0324

Table A.11: The sum of squared errors (SSE) between kMC predictions and the extent of ion-exchanged to Pt^{2+} (Moliner et al.¹) during the temperature ramp for the supported particle model with $\bar{x} = 1.5$ nm under different $\gamma_{avg,Pt}$ and $\Delta G_{monomer}^{form}$.



Figure A.20: Unsupported particle free energy model's predictions of (a) extent of ion-exchange, (b) Pt-Pt coordination number, and (c-e) particle size distributions as a function of time for the stepped temperature hold experiments. Simulation results are based on the temperature ramp-fitted $\Delta G_{\text{monomer}}^{form}$ and $\gamma_{\text{avg,Pt}}$ values for $\bar{x} =$ (c) 0.5, (d) 0.75, and (e) 1.0 nm, which are depicted by pink, purple, and blue, respectively. The grey points represent experimental data from Moliner et al.¹



Figure A.21: Supported particle free energy model's predictions of (a) extent of ion-exchange, (b) Pt-Pt coordination number, and (c-g) particle size distributions as a function of time for the stepped temperature hold experiments. Simulation results are based on the temperature ramp-fitted $\Delta G_{\text{monomer}}^{form}$ and $\gamma_{\text{avg,Pt}}$ values for $\bar{x} =$ (c) 0.5, (d) 0.75, (e) 1.0 nm, (f) 1.25, and (g) 1.5 nm, which are depicted by yellow, brown, tan, orange, and salmon, respectively. The grey points represent experimental data from Moliner et al.¹



Figure A.22: Initial particle size distributions explored during kinetic parameter fittings overlaid with the TEM experimental particle size distributions (green histogram) reported by Moliner et al.¹ The plots show supported particles with $\bar{x} =$ (a) 0.5 nm, (b) 0.75 nm, (c) 1.0 nm, (d) 1.25 nm, and (e) 1.5 nm, and unsupported particles with $\bar{x} =$ (f) 0.5 nm, (g) 0.75 nm, and (h) 1.0 nm distributions.

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Appendix B

Ostwald ripening sintering model for Pd particles on Al_2O_3 .

B.1 Introduction

This section derives the governing equations to explain the Ostwald ripening (OR) driven Pd particle sintering. These governing equations can be used for either gas phase mediated or surface mediated OR and can be modified to incorporate the support heterogeneity.

B.1.1 Two particle system

Consider a system with two particles with initial radii of R_{A0} and R_{B0} . At any given time (t), consider their particle radii to be R_A and R_B , respectively. For particle A, the rate of monomer adsorption (r_a) :

$$r_a = \beta S_A C_X \tag{B.1}$$



Figure B.1: Two particles with different sizes interacting with each other via a background monomer (X) field.

and, the rate of monomer desorption (r_d) :

$$r_d = \alpha(R_A)S_A \tag{B.2}$$

where $\alpha(R_A)$ is the functional dependence of monomer desorption (discussed later) with respect to the size, S_A is the surface area of the particle interacting with the monomer field, β is a constant depending on the collision frequency of monomers with particles, and C_X is the mean-field monomer concentration. The net growth rate of particle A is then given by:

$$\frac{dN_A}{dt} = r_a - r_d = \beta S_A C_X - \alpha(R_A) S_A \tag{B.3}$$

 N_A is the number of monomers in particle A. Similarly for particle B, we get:

$$\frac{dN_B}{dt} = \beta S_B C_X - \alpha(R_B) S_B \tag{B.4}$$

Assuming a pseudo-steady state for monomers, the net accumulation of monomers in the system is zero, and the monomer mass balance gives:

$$\frac{dN_A}{dt} + \frac{dN_B}{dt} = 0 \tag{B.5}$$

Substituting B.3 and B.4 into B.5 and solving for C_X gives:

$$C_X = \frac{\alpha(R_A)S_A + \alpha(R_B)S_B}{\beta(S_A + S_B)}$$
(B.6)

Substituting the C_X from B.6 into B.3 and B.4 cancels the β term and gives the time dependence of a number of monomers in particles A and B, respectively, as follows.

$$\frac{dN_A}{dt} = \frac{S_A S_B[\alpha(R_B) - \alpha(R_A)]}{(S_A + S_B)} \tag{B.7}$$

$$\frac{dN_B}{dt} = \frac{S_A S_B[\alpha(R_A) - \alpha(R_B)]}{(S_A + S_B)} \tag{B.8}$$

Once expressions for surface areas interacting with the monomer (S_A, S_B) and the functional form of α is determined, equation B.7 and B.8 can be solved with the initial conditions of $R_A = R_{A0}$ and $R_B = R_{B0}$ at t = 0.

B.1.2 Many particle system

Now consider a system with many (n > 2) particles interacting with each other via a monomer field of concentration C_X , as discussed above for the two-particle system. Let's denote each particle as N_i , where *i* is the number of monomers each particle consists of. Now, for any particle, the rate of monomer accumulation is given by:

$$\frac{dN_i}{dt} = \beta S_i C_X - \alpha(R_i) S_i \tag{B.9}$$

At pseudo-steady-state conditions, the monomer mass balance gives:

$$\sum_{i=1}^{n} [\beta S_i C_X - \alpha(R_i) S_i] = 0$$
 (B.10)

And solving for C_X yields:

$$C_X = \frac{\sum_{i=1}^n \alpha(R_i) S_i}{\beta \sum_{i=1}^n S_i} \tag{B.11}$$

Substituting equation B.11 into B.9 gives:

$$\frac{dN_i}{dt} = \frac{S_i \sum_{i=1}^n \alpha(R_i) S_i}{\sum_{i=1}^n S_i} - \alpha(R_i) S_i$$
(B.12)

By definition of the critical radius (R_*) ,¹ the net growth rate is zero for particles of the critical size radius. Therefore, from equation B.12:

$$0 = \frac{S_{R*} \sum_{i=1}^{n} \alpha(R_i) S_i}{\sum_{i=1}^{n} S_i} - \alpha(R_*) S_{R*}$$
(B.13)

Cancelling $S_{R*} \neq 0$ from the B.13 gives:

$$\alpha(R_*) = \frac{\sum_{i=1}^{n} \alpha(R_i) S_i}{\sum_{i=1}^{n} S_i}$$
(B.14)

This equation B.14 allows to rewrite the equation B.12 in a convenient form of:

$$\frac{dN_i}{dt} = [\alpha(R_*) - \alpha(R_i)]S_i \tag{B.15}$$

B.1.3 The functional form of the monomer desorption (α).

Assuming a spherical particle shape with a constant atomic volume Ω ($m^3/atom$) for metal particles the volumetric change of particles is given by:

$$\frac{dV_i}{dt} = 4\pi R_i^2 \frac{dR_i}{dt} = \Omega \frac{dN_i}{dt}$$
(B.16)

If the total surface area of the sphere is available for monomer exchange, the equation B.16 simplifies to:

$$\frac{dN_i}{dt} = \frac{S_i}{\Omega} \frac{dR_i}{dt} \tag{B.17}$$

By comparing equation B.15 and B.17 we get:

$$\frac{dR_i}{dt} = \Omega[\alpha(R_*) - \alpha(R_i)]$$
(B.18)

The sintering model developed by Wynblatt and Gjostein was later modified using the exact form of the Gibbs-Thompson (GT) particle free energy model by Parker and Campbell [2] to yield the following sintering equation for the time evolution of the radius of particles.

$$\frac{dR_i}{dt} = \frac{K''}{R_i} \exp\left(\frac{-E_{tot.}}{k_B T}\right) \left[\exp\left(\frac{2\gamma_m \Omega}{k_B T R_*}\right) - \exp\left(\frac{2\gamma_m \Omega}{k_B T R_i}\right)\right]$$
(B.19)

Where K'' is a constant, $E_{tot.}$ is the sum of all the activation energies required for monomer generation and adsorption, and γ_m is the surface energy of the metal. By comparing equations B.18 and B.19, we can deduce the functional form of $\alpha(R)$ for a constant temperature and γ_m .
$$\alpha(R) = \frac{K''}{R} \exp\left(\frac{-E_{tot.}}{k_B T}\right) \left[\exp\left(\frac{2\gamma_m \Omega}{k_B T R}\right)\right] = \frac{K'}{R} \left(\exp(\frac{L}{R})\right) \tag{B.20}$$

Here, $L = \frac{2\gamma_m \Omega}{k_B T}$ is a constant commonly referred to as the capillary length,¹ and it depends on the surface energy of particles (γ_m) , temperature (T), and atomic volume (Ω) of the material as expressed in equation B.21. K' (m⁻¹s⁻¹) is another constant that depends on temperature and the total activation energy of monomer generation and adsorption. Parker and Campbell² considered only the perimeter of particles as available for monomer exchange (this assumption may be more appropriate for the surface-mediated OR than for the gas phase mediated OR), yielding the 1/R term in the prefactor in the equation B.20. However, in our simple model, which assumes the total surface area is available for monomer exchange, the $\alpha(R)$ can be expressed as:

$$\alpha(R) = K \exp\left(\frac{L}{R}\right) \tag{B.21}$$

B.1.4 Numerical simulations for two particle system

We numerically solved equations B.7 and B.8 using the functional form of equation B.21 for the spherical two-particle system. We used arbitrary values for $N_{A0} = 200$, $N_{B0} = 300$, $K = 10^{-1}$ m⁻²s⁻¹, and L = 1 nm for the simulation results shown Figure B.2.

Figure B.2 shows that the larger particle grows until the smaller particle is annihilated, as expected from the typical OR sintering model. Further, the total number of monomers is conserved in A and B particles as expected.

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Figure B.2: Number of monomers over time in two particles (A-blue and B-orange) with different sizes interacting with each other. The total number of monomers in the system is plotted in green.

B.1.5 Numerical simulations for multi-particle system

For a multiparticle system, we initiated the simulation by randomly generating the initial particle size distribution from the statistics gathered using TEM particle size measurements (e.g. Figure B.3, Figure B.4). Next, we assumed a spherical shape for Pd particles for simplicity, and the number of monomers in a given particle size can be estimated using the Pd atomic volume. Next, for a given K and L parameter combination, the coupled differential equations (B.14-B.15) can be solved for each particle. We integrated equations using the RK45 method with the $solve_ivp$ function as implemented in the SciPy package in Python. The system of ODEs are deterministic, however, for a given statistical average and standard deviation of particles, the initial partice size distributions (randomly generated) are different for each simulation. Therefore, multiple simulations (with the same parameter set and particle size distribution statistics) can be averaged to produce better statistics



Figure B.3: Initial particle size distribution (PSD) from ex-situ TEM images of the Pd-LND-2.3 nm/Al₂O₃. The total number of particles imaged (N), the average of particle sizes ($\mu_{\rm ND}$), and the standard deviation of the particle sizes ($\sigma_{\rm ND}$) and log-normal distribution parameters ($\mu_{\rm LND}$ and $\sigma_{\rm LND}$) are reported in the upper right corner. The corresponding normal distribution and log-normal distributions are shown in solid and dashed black, respectively.

for size distributions. We averaged 100 independent simulations for the simulations (Figure B.5). Next, we used a grid search to find K and L parameter combinations that minimize the error between experimental and simulated average particle size.

B.1.6 Extending the model for a heterogeneous support with two types of metal-support interaction strengths.

For homogeneous support, all particles experience the same metal-support interaction, and therefore, K and L parameters for each particle are the same. However, the local environment of each Pd nanoparticle could be different, yielding variations of sintering parameters (K and L). As a first approximation, now consider two types of metal-support interactions and, therefore, two sets of sintering parameters (K_1 , L_1



Figure B.4: Initial particle size distribution (PSD) from ex situ TEM images of the Pd-ND-2.4 nm/Al₂O₃. The total number of particles imaged (N), the average of particle sizes ($\mu_{\rm ND}$), and the standard deviation of the particle sizes ($\sigma_{\rm ND}$) and log-normal distribution parameters ($\mu_{\rm LND}$ and $\sigma_{\rm LND}$) are reported in the upper right corner. The corresponding normal distribution and log-normal distributions are shown in solid and dashed black, respectively.

and K_2 , L_2).³ These two regions of the support could be either separated from each other so that they do not exchange monomers (or very slow monomer exchange) or can interact with each other via rapid monomer exchange. In the following discussion, we refer to the former scenario of monomer generation and transport on a heterogeneous metal-support as uncoupled and the latter as coupled. For both scenarios, the simulations can be initiated with the required proportions of metal particles (*n* and *m*) in each region.

B.1.6.1 Uncoupled monomer transport in two regions.

In this case, the governing equations (B.11–B.12) can be directly applied recursively to the two regions with their respective sintering parameters (K_1 , L_1 and K_2 , L_2).



Figure B.5: Simulated evolution of average particle size with time assuming a homogeneous support (same parameter values for all particles) for oxidative ($L = 0.1 \text{ nm}, K = 3 \times 10^{-2} \text{ m}^{-2} \text{s}^{-1}$) and reductive ($L = 1.5 \text{ nm}, K = 2.5 \times 10^{-2} \text{ m}^{-2} \text{s}^{-1}$) aging conditions. Experimental data (from O₂ chemisorption) for Pd-2.3LND-Al₂O₃ are shown with circular markers with error bars representing the standard deviation of three measurements.

B.1.6.2 Coupled monomer transport in two regions.

In this case, the equations (B.11-B.12) need to be modified as the monomer field is common for both regions. Denoting particles in two regions with i and j indices, equation B.10 becomes:

$$\sum_{i=1}^{n} [\beta S_i C_X - \alpha(R_i) S_i] + \sum_{j=1}^{m} [\beta S_j C_X - \alpha(R_j) S_j] = 0$$
(B.22)

Here, n and m are the number of Pd particles in each region i and j, respectively. Solving the equation B.22 for C_X yields:

$$C_X = \frac{\sum_{i=1}^n \alpha(R_i) S_i + \sum_{j=1}^m \alpha(R_j) S_j}{\beta \sum_{i=1}^n S_i + \beta \sum_{j=1}^m S_j}$$
(B.23)



Figure B.6: Simulated evolution of average particle size with time assuming a homogeneous support (same parameter values for all particles) for oxidative $(L = 0.1 \text{ nm}, K = 3 \times 10^{-2} \text{ m}^{-2} \text{s}^{-1})$ and reductive $(L = 1.5 \text{ nm}, K = 2.5 \times 10^{-2} \text{ m}^{-2} \text{s}^{-1})$ aging conditions. Experimental data (from O₂ chemisorption) for Pd-2.4ND-Al₂O₃ are shown with square markers with error bars representing the standard deviation of three measurements.

Substituting equation B.22 into B.23 gives:

$$\frac{dN_i}{dt} = S_i \frac{\sum_{i=1}^n \alpha(R_i) S_i + \sum_{j=1}^m \alpha(R_j) S_j}{\sum_{i=1}^n S_i + \sum_{j=1}^m S_j} - \alpha(R_i) S_i$$
(B.24)

This is the governing equation for the n particles in region i and similarly for the remaining m particles in region j the governing equation is:

$$\frac{dN_j}{dt} = S_j \frac{\sum_{i=1}^n \alpha(R_i) S_i + \sum_{j=1}^m \alpha(R_j) S_j}{\sum_{i=1}^n S_i + \sum_{j=1}^m S_j} - \alpha(R_j) S_j$$
(B.25)

Then, the equations (B.23–B.25) can be solved numerically with their respective sintering parameters $(K_1, L_1 \text{ for region } i \text{ and } K_2, L_2 \text{ for region } j)$.

B.1.7 DFT calculations for binding energy estimations.

We considered $Pd(OH)_2$ binding energy on γ/Al_2O_3 using the following equation:

$$\operatorname{Al}_{x}\operatorname{O}_{y}\operatorname{H}_{z} + \operatorname{Pd}(\operatorname{OH})_{2}(g) \xrightarrow{\Delta E} \operatorname{Al}_{x}\operatorname{O}_{y}\operatorname{H}_{(z-2)}\operatorname{Pd} + 2\operatorname{H}_{2}\operatorname{O}$$
(B.26)

The surface models were taken from a previous study of Ag on $\gamma/\text{Al}_2\text{O}_3^4$ and Pd was systematically (using a library of initial guesses) placed on each surface and grain boundaries. The most exothermic binding energy calculated using Pd(OH)₂(g) reference state (equation B.26) for each support location is shown in Table *B*.1.

γ/Al_2O_3 Binding site location	Most exothermic binding energy ΔE (kJ mol Pd ⁻¹)
110	-61.0
100	-59.7
111	-32.0
(110)-(100)	-198. 1
(100)-(111)	Does not anchor $Pd(OH)_2(g)$ exothermically
(110)-(111)	-138. 1

Table B.1: ΔE in kJ mol Pd⁻¹ calculated for different locations in the $\gamma/\text{Al}_2\text{O}_3$ support.

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