

## ABSTRACT

### Influence of Metal Speciation and Support Properties for Ammonia Oxidation and Other Automotive Exhaust Catalytic Applications

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Metal speciation and structure can be influenced by the metal deposition method, interactions with the support, and by the specific post-deposition treatments and reaction conditions experienced during its lifetime of carrying out a desired catalytic application. Supported metal particles with varying size contain different surface structures and atomic coordination environments, which not only may influence reaction rates but also the interconversion between agglomerated metallic domains and highly dispersed cationic metal sites. Here, we address the influence of post-deposition treatments and support properties on structural interconversion of Pd and Cu on aluminosilicate chabazite (CHA) zeolites, Pt on gamma-alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), and Pd on amorphous oxide supports ( $\gamma\text{-Al}_2\text{O}_3$ , La-doped  $\text{Al}_2\text{O}_3$ , and  $\Theta\Delta\text{-Al}_2\text{O}_3$ ). The fundamental insights from these studies can be applied to the rational design of catalysts used widely in automotive exhaust aftertreatment systems, including Pd-exchanged zeolites for passive  $\text{NO}_x$  ( $x = 1,2$ ) adsorbers (PNA), Cu-exchanged zeolites for  $\text{NO}_x$  ( $x = 1,2$ ) selective catalytic reduction (SCR), Pt- $\text{Al}_2\text{O}_3$  for  $\text{NH}_3$  slip applications, and supported Pd materials for three-way catalysts (TWC).

Incipient wetness impregnation (IWI) and colloidal Pd nanoparticle syntheses with deposition on CHA zeolites were used to prepare materials with distinct Pd nanoparticle sizes and distributions. These Pd-CHA samples were used to isolate the effects of Pd particle size distributions on structural interconversion between ion-exchanged Pd and agglomerated Pd domains under realistic operating conditions. Small Pd nanoparticles (2 nm) had larger fractions of agglomerated Pd that were converted to ion-exchanged  $\text{Pd}^{2+}$  sites than large Pd nanoparticles (7 and 14 nm) at fixed air treatment temperatures (598–973 K) and  $\text{H}_2\text{O}$  pressures (2–6 kPa  $\text{H}_2\text{O}$ ), consistent with computational thermodynamic calculations. Furthermore, the addition of  $\text{H}_2\text{O}$  to the treatment of different Pd nanoparticles (2–14 nm) inhibited the formation of ion-exchanged  $\text{Pd}^{2+}$  (thermodynamics), but not the rate of redispersion (kinetics). This demonstrates, regardless of Pd nanoparticle size, water vapor in the automotive exhaust streams will facilitate sintering of metal species in PNA applications.

Aqueous-phase exchange of Cu on CHA zeolites with varying support properties (i.e., number of paired Al sites in the 6 membered ring) were used to prepare materials with distinct types and numbers of extraframework Cu species ( $\text{Cu}^{2+}$ ,  $\text{CuOH}^+$ ). These Cu-CHA materials can be used to analyze Cu site structural changes before and after exposure to hydrothermal aging conditions. In the absence of water, some  $\text{Cu}^{2+}$  sites condense to form binuclear  $\text{O}_x$ -bridged Cu species that can be reduced with  $\text{H}_2$  to form Cu-hydride sites and reject  $\text{H}_2\text{O}$ , leading to a sub-stoichiometric  $\text{H}_2$  consumption ( $\text{H}_2/\text{Cu} < 0.5$ ). In the presence of water, all nominally isolated  $\text{Cu}^{2+}$  species can convert to  $[\text{CuOH}]^+$  structures, which can subsequently be reduced by  $\text{H}_2$  to form a Cu-hydride and reject  $\text{H}_2\text{O}$ , leading to stoichiometric  $\text{H}_2$  consumption ( $\text{H}_2/\text{Cu} \sim 0.5$ ). Furthermore, the presence of water led to reduction features in  $\text{H}_2$  temperature programmed reduction (TPR)

profiles that were similar among Cu-CHA materials, regardless of the initial Cu speciation present after high temperature oxidation treatments, further supporting the proposal that all nominally isolated  $\text{Cu}^{2+}$  sites convert to a similar structure (e.g.,  $[\text{CuOH}]^+$ ). This demonstrates how water influences Cu speciation on CHA materials of varying origin or treatment history, aiding in quantifying SCR-active isolated Cu ions and SCR-inactive Cu species (e.g.,  $\text{CuO}$ ,  $\text{CuAl}_2\text{O}_4$ ).

Materials containing Pt supported on  $\gamma\text{-Al}_2\text{O}_3$  were prepared with different average Pt particle sizes (2–13 nm) by increasing the temperature of post-deposition treatment in air (523–873 K). This suite of materials was interrogated to isolate the effects of Pt particle size on  $\text{NH}_3$  oxidation rates and selectivities during conditions relevant to  $\text{NH}_3$  slip applications in diesel exhaust aftertreatment. For all Pt particle sizes,  $\text{NH}_3$  oxidation rates displayed a hysteresis with temperature, with high rates measured during temperature decreases than during temperature increases. Small Pt particles (2 nm) had lower rates (per surface Pt, quantified by CO chemisorption) than large Pt particles (13 nm), signifying that  $\text{NH}_3$  oxidation is a structure-sensitive reaction. Furthermore, the surfaces of supported Pt particles were shown to restructure under  $\text{NH}_3$  oxidation reaction conditions, influencing the effective Pt oxidation state, surface structure (number and type of exposed Pt sites), and surface coverages of intermediates leading to the observed rate hysteresis phenomenon. This demonstrates Pt particles undergo dynamic structural changes during reaction that influences the ability to convert  $\text{NH}_3$  to environmentally benign products in  $\text{NH}_3$  slip applications.

The influence of treatment conditions, support properties, and initial Pd particle size and distribution on the kinetics of nanoparticle sintering were investigated to identify the material properties most influential for maintaining high dispersion to maximize metal utilization for three way catalysts (TWC) during the conversion of governmentally regulated pollutants, carbon monoxide (CO), unburned hydrocarbons (HC), and  $\text{NO}_x$ . Pd was deposited by conventional IWI methods to generate polydisperse particle size distributions, and by first preparing colloidal Pd nanoparticle solutions of monodisperse particle size distribution, onto various supports ( $\gamma\text{-Al}_2\text{O}_3$ , La-doped  $\text{Al}_2\text{O}_3$ ,  $\Theta\Delta\text{-Al}_2\text{O}_3$ ) and subjected to aging under oxidative and reductive conditions relevant for aging conditions experienced during TWC operation. The average Pd particle size for all Pd-supported materials increased with increasing treatment time for both reductive and oxidative treatments. For samples prepared with IWI (i.e., log normal distribution of Pd particle sizes), reductive aging treatments led to higher sintering rates than oxidative treatments. In contrast, for samples prepared using colloidal Pd solutions (i.e., normal distribution of Pd particle sizes), oxidative aging treatments led to higher sintering rates than reduction treatments. Furthermore, under the same treatment condition and time, samples prepared with IWI resulted in higher average Pd particle sizes. These results indicate that more monodisperse initial Pd particle size distributions are beneficial for lowering sintering rates, providing guidance for the design of supported metal catalysts for TWC applications with improved metal utilization during their lifetimes.

Here, the combination of synthesis approaches to prepare a suite of model (e.g., powder) supported metal catalysts of systematically varying structure and composition, interrogated using site and structural characterizations and steady-state and transient kinetic measurements, along

with predictions from theoretical calculations, enabled disentangling the influence of material properties and gas environments that affect metal speciation, structure, and oxidation state in real-world aftertreatment systems that use more complex catalytic architectures (e.g., layered washcoats) and reactor designs (e.g., monoliths). This approach provides insights into the fundamental thermodynamic and kinetic factors influencing metal restructuring and interconversion under realistic conditions encountered in automotive exhaust aftertreatment applications, and the kinetic and mechanistic factors that underlie complex phenomena (e.g., reaction rate hysteresis) from data measured in the absence of hydrodynamic artifacts. The overall approach used in this work enabled development of synthesis-structure-function relationships on various metal supported catalysts for automotive exhaust aftertreatment applications, which can provide guidance for material design and treatment strategies to form and retain desired metal structures throughout the material lifetime, including synthesis, reaction, and regeneration treatments.