ABSTRACT

Lardinois, Trevor M. Ph.D., Purdue University, June 2021. Synthesis and Characterization of Metal-Exchanged Zeolite Materials for Automotive Exhaust Aftertreatment. Major Professors: Rajamani Gounder and Fabio H. Ribeiro.

Metal-zeolites are promising materials for passive adsorber technologies for the abatement of nitrogen oxides (NOx, x = 1,2) and aldehydes during low-temperature operation in automotive exhaust aftertreatment systems. The aqueous-phase exchange processes used commonly to prepare metal-zeolites typically require mononuclear, transition metal complexes to diffuse within intrazeolite pore networks with their solvation shells and replace extraframework cations of higher chemical potential. When metal complexes are larger than the zeolite pore-limiting diameter, this imposes intracrystalline transport restrictions; thus, complexes and agglomerates tend to preferentially deposit near the surfaces of crystallites, requiring post-synthetic treatments to disperse metal species more uniformly throughout zeolite crystallites via solid-state ion-exchange processes. Here, we address the influence of post-synthetic gas treatments and zeolite material properties on the structural interconversion and exchange of extraframework Pd in CHA zeolites with a focus on the thermodynamic, kinetic, and mechanistic factors that dictate the Pd site structures and spatial distributions that form.

Pd-amine complexes introduced via incipient wetness impregnation on CHA zeolites were found to preferentially site near crystallite surfaces. Post-synthetic treatments in flowing air results in Pd-amine decomposition and agglomeration to metallic Pd^0 and subsequent oxidation to PdO, before converting to mononuclear Pd^{2+} cations through an Ostwald ripening mechanism at high temperatures (>550 K). Progressively higher air treatment temperatures (up to 1023 K) were found to (1) thermodynamically favor the formation of mononuclear Pd^{2+} cations relative to agglomerated PdO particles, (2) increase the apparent rate of structural interconversion to mononuclear Pd^{2+}, and (3) facilitate longer-range mobility of molecular intermediates involved in Ostwald ripening processes that allow Pd cations to

form deeper within zeolite crystallites, resulting in more uniformly dispersed Pd-zeolite materials. Additionally, the controlled synthetic variation of the atomic arrangement of 1 or 2 Al sites in the 6-membered ring of CHA was used to show a thermodynamic preference to host mononuclear Pd^{2+} cations charge-compensated by 2 Al sites over $[PdOH]^{+}$ complexes at 1 Al site. Colloidal Pd nanoparticle syntheses and deposition methods were used to prepare monodisperse Pd-CHA materials to isolate the effects of Pd particle size on structural interconversion to mononuclear Pd^{2+} under a range of external environments. Consistent with computational thermodynamic predictions, smaller Pd particle sizes favor structural interconversion to mononuclear Pd^{2+} under high-temperature air treatments (598–973 K), while adding H_2O to the air stream inhibits the thermodynamics but not the kinetics of mononuclear Pd^{2+} formation, demonstrating that water vapor in exhaust streams may be deleterious to the long-term stability of Pd-zeolite materials for passive NOx adsorption.

The influence of metal-zeolite material properties on the adsorption, desorption, and conversion of formaldehyde, a government-regulated automotive pollutant, under realistic conditions was investigated to identify beneficial material properties for this emerging application in mobile engine pollution abatement. A suite of Beta zeolite materials was synthesized with varied adsorption site identity (Brønsted acid, Lewis acid, silanol groups, and extraframework metal oxide) and bulk site densities. All materials stored formaldehyde and converted a large fraction of formaldehyde to more environmentally benign CO and CO_2, demonstrating the efficacy of silanol defects and zeolitic supports for the storage of formaldehyde. Sn-containing zeotypes, containing either Lewis acidic framework Sn sites or extraframework SnO_x particles, resulted in the greatest selectivity to CO and CO_2 formed during formaldehyde desorption, suggesting that Sn species are a beneficial component in metal-zeolite formulations for the abatement of formaldehyde in automotive exhaust streams.

Together, this work demonstrates how the combining the precise synthesis of metal-zeolites of varied bulk and atomic properties with site-specific characterization and titration methods enables systematically disentangling the influence of separate material properties

(e.g., Pd particle size, zeolite framework Al arrangement, silanol density, heteroatom identify) and external environment on changes to metal structure, speciation, and oxidation state. This approach provides thermodynamic, kinetic, and mechanistic insights into the factors that influence metal restructuring under the practical conditions encountered in automotive exhaust aftertreatment applications and guidance for materials design and treatment strategies to form desired metal structures during synthesis and after regeneration protocols.