

Kinetics of site transformations in Pd/AEI zeolite for NO_x adsorption

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Significance and Relevance

Pd ion exchanged into BEA, ZSM-5, SSZ-13 or AEI zeolite are contenders in passive NOx adsorber (PNA) technologies for diesel exhaust gas aftertreatment under cold start conditions^{1,2}. However, water and CO-induced Pd agglomeration into clusters and nanoparticles decreases the number of active Pd sites available for NO adsorption. The combination of lab experiments and kinetic modelling allows us to build a physically relevant, predictive model of PNA activity and adsorption capacity depending on the trajectory of operating conditions (temperature, water content, CO and NO concentration), and to explore possible catalyst reactivation strategies for improved performance of the catalyst under real world conditions.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, Air cleaning and combustion Preferred presentation: Oral preferred

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Introduction and Motivations

In passive NO_x adsorber (PNA), NO is adsorbed at low temperature and released once the exhaust temperature is warm enough for downstream SCR catalysts to be active. Pd interconverts between single atoms and clusters within zeolites depending on the operating conditions. Pd has been described as water-solvated and detached from the zeolite at low temperature, while under dry conditions or at higher temperatures, the Pd is associated with the zeolite³. Furthermore, reduction of Pd ions into the metallic state promotes their agglomeration, hence the effect of reducing agents such as CO on Pd clusters formation and growth of larger Pd nanoparticles outside the zeolite framework must be considered. Pd agglomeration decreases the number of active Pd sites available for NO adsorption, and strategies for slowing down or even reversing this process must be developed. When oxidized, small Pd particles can either disintegrate and reform the ion-exchanged species or agglomerate and form larger particles that reside on the external of the zeolite⁴.

Kinetic modeling allows calculation of reaction rates under a variety of exhaust gas conditions so that conversion and overall emissions reduction performance can be computationally predicted. Standard kinetic models, however, use fixed values of kinetic parameters for the given catalyst. Expanding the models to include how the catalyst active sites evolve is critical. This means including rate laws for changes in active site concentrations as a function of reaction environment conditions.

Materials and Methods

A model 1% Pd/AEI catalyst was prepared by incipient wetness impregnation of Pd nitrate into AEI zeolite with Si-to-AI ratio 20, followed by 2 h of calcination at 500 °C and 16 h of high-temperature treatment at 750 °C in air, resulting in Pd ions exchanged inside the zeolite structure. STEM images showed no Pd nanoparticles present in the prepared catalyst. H₂ temperature programmed reduction has been used to characterize the amounts of ion-exchanged and PdO particles, and NO adsorption with temperature-programmed desorption were used to quantify the number of active Pd sites in the zeolite framework.

Each PNA experiment was performed with 0.4g of the catalyst powder in a tubular lab reactor. The feed always contained 5% O_2 , 5% or 10% H_2O and 10% CO_2 and the total flow rate was 2 dm³/min. The test included isothermal NO adsorption at 100°C, desorption temperature ramp to 500°C, cooling



down, 5 or 20 min deactivation period at various temperatures, CO, NO and H_2O levels, and repeated NO adsorption and temperature programmed desorption. Finally, the possibility of catalyst reactivation by Pd redispersion in the zeolite structure was tested under oxidizing conditions at 500 °C and 750°C.



Results and Discussion

Figure 1. Change in NO adsorption capacity due to Pd agglomeration during 20 min in Pd/AEI zeolite at 100 °C. a) Impact of CO, H_2O and NO. b) Impact of deactivation time.

Pd agglomeration at low temperatures is accelerated by water and CO, Figure 1. The corresponding mechanism involves formation of Pd hydrates and carbonyls that allow detachment of Pd from the zeolite framework and make it mobile. The impact of CO on the process is crucial as it can reduce Pd ions into metallic state and promote the formation of Pd clusters and nanoparticles. In contrast, increased NO concentration slows down the deactivation as it competes with CO for the adsorption on Pd sites, which weakens CO impact. The deactivation rate is practically constant at temperatures 80-120 °C and effectively decreases at higher temperatures, which is caused by (i) the decreasing extent of Pd hydration that makes Pd less mobile and supports its anchoring into the zeolite framework, and (ii) the increasing CO oxidation rate that effectively consumes all CO near the inlet.

Based on the experimental data, kinetic equations for Pd sites transformation are expressed as functions of actual site concentration, gas composition and corresponding coverage on active sites, metal oxidation state and temperature. Pd cluster and nanoparticle formation and growth are affected by Pd reduction steps. The lab experiments provide data for evaluation of rate coefficients for individual site transformation steps as well as their possible reversibility under different operating conditions. While complete Pd redispersion into zeolite framework requires 750°C, partial catalyst regeneration can be achieved below 500°C.

Acknowledgements

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