

## Operando Infrared and XAS study of NO adsorption on zeolite supported palladium under complex gas feeds

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The reduction of nitrogen oxides (NO<sub>x</sub>) emissions from diesel engines is central to meeting current and future emission legislation standards. Two catalytic systems to meet these standards are commonly used today: urea based selective catalytic reduction (SCR) catalysts or NO<sub>x</sub> storage and reduction (NSR) catalysts. These technologies can achieve high NO<sub>x</sub> reduction efficiencies once they reach their operating temperature, typically above 200°C. One strategy of reducing the cold start NO<sub>x</sub> emission is to store NO<sub>x</sub> at low temperatures and then thermally release it once the downstream catalysts reach their operating temperatures. These low temperature NO<sub>x</sub> storage materials are more commonly known as passive NO<sub>x</sub> adsorbers (PNAs). Zeolite supported palladium have proved to be one of the most remarkable candidates for this application as they can adsorb NO<sub>x</sub> at temperatures below 200° C with high storage capacity and trapping efficiency [1].

The present study offers a combined Infrared and XAS approach under operando conditions to understand the NO storage mechanism on zeolite supported palladium. The samples employed in the study are 0.5 wt% palladium on chabazite (CHA) and beta zeolite (BEA) – representing small and large pore zeolites respectively - and 0.5 wt% palladium on alumina for comparison. The samples were prepared by incipient wetness impregnation.

Operando diffuse reflectance infrared experiments were performed in a Harrick Praying Mantis diffuse reflectance cell, using a Perkin Elmer Frontier spectrophotometer. Operando XAS measurements were performed in a capillary cell with a hot air blower, at the palladium K-edge (24.35 keV) on the SuperXAS beamline at the Swiss Light Source. Both sets of experiments were monitored by mass spectrometry. The properties of the materials were initially evaluated in a simplified gas mixture. Stepwise other gases were added, leading towards a synthetic gas mixture that simulated cold start exhaust emissions from typical diesel vehicles (NO; CO; O<sub>2</sub>; H<sub>2</sub>O). Thus influence of each gas feed component was monitored during storage at 100°C, and during release between 100 and 400°C.

The combination of operando techniques has provided understanding of adsorbed surface species as well as the nature of palladium active sites during storage and release cycles. It has been shown that palladium on a zeolite support is mostly present in the dispersed form at exchange sites, and is responsible for NO adsorption. This large cationic component is also resistant to reduction [2]. The results further reveal a unique characteristic: exchanged palladium cations continue to maintain their location without chemical transformation during storage under the complex gas feed. This insight has helped establish the structural requirements for this critical emission control process.

[1] R.R. Rajaram, H.Y. Chen, D. Liu, U.S. Patent Application 14/563, 340 (2014)

[2] H.Y. Chen, J.E. Collier, D. Liu, L. Mantaroşie, D. Duran-Martin, N. Novak, R. Rajaram, D. Thompsett, *Catalysis Letters*, 146, 1706 (2016)