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## Publishable summary

With the increase in automotive market, the concerns for nitrogen oxides ($NO_x$) generation substantially grows in many countries. The application of technologies such as lean $NO_x$ traps (LNT) and $NH_3$ selective catalytic reduction (SCR) can significantly reduce vehicle $NO_x$ emissions. However, owing to the kinetic limitations of the LNT and that urea cannot be dosed at low temperature for the SCR system (around 200 $^oC$ is typically needed), these systems cannot effectively reduce $NO_x$ emissions in cold start periods of the engine. Accordingly, passive $NO_x$ adsorption (PNA) has been recently developed as a promising technology for controlling the $NO_x$ emissions during the cold start period. Three material groups have been studied in detail for PNA application: $Pd/Al_2O_3$, $Pd/CeO_2$ and Pd/Zeolites, where all of these materials showed significant $NO_x$ storage capacity at low temperature. However, both $Pd/Al_2O_3$ and $Pd/CeO_2$ suffers from serious degradation with the existence of sulphur, which significantly weaken the interaction between PdO and support. Therefore, there is a growing interest in Pd zeolites for PNA due to their tolerance to sulphur and $H_2O$. Pd/ZSM-5, Pd/BEA and Pd/SSZ-13 have been widely investigated as high-performance PNA materials. Particularly, SSZ-13 zeolite, which has small pore in the internal channel, has been shown to be most effective material among all the zeolites, with a relatively high $NO_x$ desorption temperature. However, the PNA module is usually designed to be placed in front of the other aftertreatment modules to adsorb $NO_x$ species. Owing to the incomplete combustion of diesel during cold start, CO pulses with extremely high concentrations are generated, which can account for 80% of CO release in the total duration.  Under such high concentration CO, serious degradation usually happens on PNAs during the multiple times cold start of engine.

To investigate the reaction mechanism of PNA, a few kinetic models have been developed, while there are no available kinetic models for the effect of $NO_x$ and CO concentrations on Pd/SSZ-13. We first illustrate a CO-assisted mechanism in this program by combining experimental and kinetic modelling studies. Pd/SSZ-13 has been synthesized, characterized, and evaluated as a PNA in low-temperature $NO_x$ adsorption and temperature program desorption cycles, to represent multiple cold start periods. The gas compositions were also systemically changed, where both the effect of varying $NO_x$ and CO feed was evaluated in the presence of high water and oxygen contents. A kinetic model was developed to simulate the profiles of NO and $NO_2$, including three initial Pd sites ($Z^-Pd(II)Z^-$, $Z^-[Pd(II)OH]^+$ and PdO). It is concluded from X-ray photoelectron spectroscopy and in-situ Diffuse Reflection Infrared Fourier Transformations Spectroscopy, flow reactor measurements and modelling observations that CO reduces Pd(II) species to Pd(I)/Pd(0) species, which increases the stability of the stored NOx species, resulting in a release above the urea dosing temperature. The model could well describe the experimental features, including the effect of CO. In addition, the model was used for full-scale catalytic converter simulations.

Although the kinetic models for the effect of $NO_x$ and CO concentrations are established, the influence of CO is still questionable. Experimentally we find an irregular effect by changing CO concentration: Under low CO concentration (0~400 ppm), CO contributes to the larger amount of absorbed $NO_x$ and a higher temperature for desorption, while a substantial degradation of the Pd zeolite occurs during multi-cycle $NO_x$ adsorption under high CO concentration (~4000 ppm). Owing to the very different

influences of CO under varied concentrations on Pd zeolite, no kinetic model has been established so far that could be applied for describing the CO-assisted $NO_x$ storage and CO-induced Pd zeolite deactivation. Herein, we illustrate the CO-induced degradation mechanism of Pd zeolite by combining experiments and kinetic models. Pd/SSZ-13 has been used in multicycle processes containing $NO_x$ adsorption at low temperature and temperature programmed desorption, which represents the PNA degradation in multiple cold start periods. A kinetic model was developed to describe the $NO_x$ storage and degradation behaviour of Pd/SSZ-13. Both experimental and modelling observations suggested that two Pd sintering modes are occurring under high CO concentration, namely Ostwald ripening and particle migration. Apart from the degradation behaviour, this model is also adequate for describing multi-cycle $NO_x$ storage and release behaviour under low CO concentration.

Based on the CO-induced degradation mechanism, we further developed a novel form of Pd/SSZ-13. This Pd/SSZ-13 showed a better stability than the sample synthesized by the common process. Several characterizations were conducted to determine why the newly synthesized Pd/SSZ-13 exhibited a higher stability.  This material offers a potentially improved stability of PNAs under extremely high CO concentration pulses from incomplete diesel combustion during engine cold start.

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