Pd-promoted Beta Zeolite for Passive NOx Adsorber Applications

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Introduction

- To meet forthcoming U.S. Tier 3 emission standards, the abatement of NOx emissions in lean exhaust during engine cold starts will be essential.
- One potential option is the use of a passive NOx adsorber (PNA) device combined with a downstream urea-SCR catalyst [1]. In this system, the PNA adsorbs NOx emitted from the engine during cold starts, and then releases the NOx at higher temperatures, e.g., above 200 °C. At this point the downstream SCR catalyst is sufficiently warm to function efficiently.
- Pd-zeolite PNAs have attracted significant interest since Chen et al. reported their remarkable NOx adsorption performance at low temperature [2]. The goal of this study is to understand the nature and function of the Pd species in Pd-Beta zeolite during NOx adsorption and desorption.

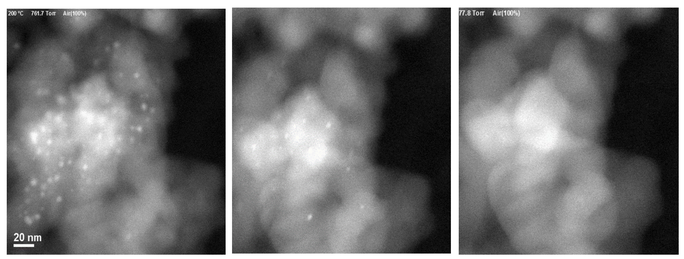
Experimental

- Two NH_4-BEA zeolites with different Si/Al ratios (12.5 and 19; Zeolyst International) were employed in this study. A series of Pd-promoted Beta zeolites were prepared by incipient wetness impregnation with aqueous $Pd(NH_3)_4](NO_3)_2$, which are hereafter designated as xPd-BEA (x representing the weight percent Pd loading). For comparison purposes, H-Beta (H-BEA) and 1.0 wt% Pd-promoted Si-Beta (1.0 Pd-Si-BEA) samples were also included in this study.
- NOx adsorption-desorption measurements were conducted in a microreactor equipped with an MS (QMS 200). 100 mg of sample was pretreated at 500 °C in 10% O_2/He flow prior to NOx storage at 50 °C in a feed containing 1000 ppm NO, 10% O_2, He bal. (unless otherwise stated). Subsequent NOx desorption used a ramp of 10 °C/min in either He (for ads. w/o O_2 added) or O_2 after extended purging at the adsorption temperature (1 h).
- DRIFTS measurements were used to study NOx adsorption-desorption behavior and the dependence on Pd oxidation state.

Results and Discussion

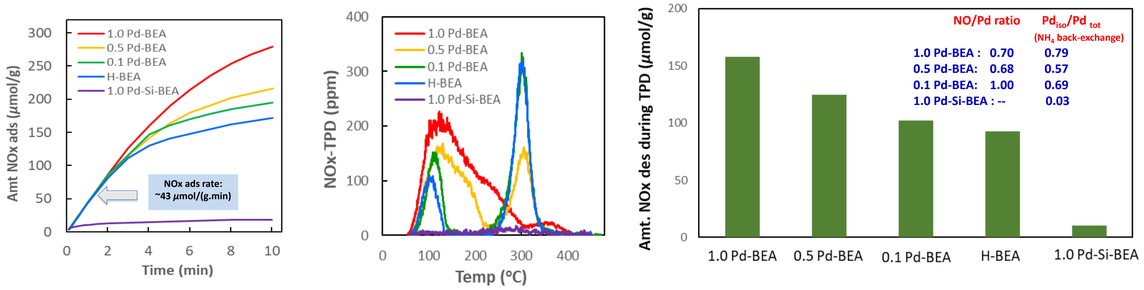
1. Pd distribution studied by HRTEM (treated in flowing air)

200°C 550°C 750°C



- **RT and 200 °C**: Observation of finely distributed Pd nanoparticles. H_2-TPR indicated ~68% of total Pd present as isolated (ion-exchanged) Pd, ~79% obtained by NH_4^+ back ion-exchange.
- **550 °C**: Coarsening/clustering of Pd particles by consumption of nanoparticles.
- **750 °C**: Further dissolution of small Pd particles while others coarsen (not shown here). H_2-TPR indicates 95% ion-exchanged Pd.

2. Effect of Pd loading (Si/Al=12.5)



NOx adsorption:

- Regardless of Pd loading, the NOx uptake rate for the first 2 min was very similar (ca. 43 μmol/(g.min)).
- NOx uptake during 10 min period increased with Pd loading. In contrast, Pd-Si-BEA (w/o Al) showed almost no NOx uptake.

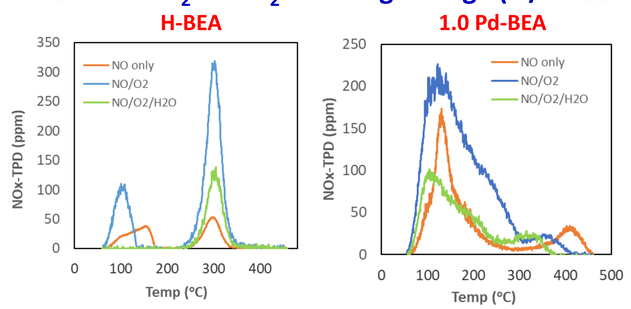
NOx-TPD:

- **H-BEA:** two distinct NOx desorption peaks at *ca*. 100 and 300 °C
- **Pd-BEA**: compared to H-BEA, the low-temp peak became more intense with a shoulder around 250 °C. The high-temp peak became weak and almost disappeared at a Pd loading of 1.0 wt%.
- **Pd-Si-BEA:** negligible NOx release during TPD.

Overall Performance:

- **Pd utilization**: estimated by NO/Pd ratio, which is calculated by taking the difference in the amount of NOx desorbed during TPD between Pd- and H-BEA divided by the amount of Pd loaded. 1.0 Pd-BEA and 0.5 Pd-BEA: ca. 70 % of Pd utilized for NOx ads.; 0.1 Pd-BEA: complete utilization of Pd for NOx storage.
- **Correlation of NO/Pd ratio with Pd_{iso}/Pd_{tot}** : indicates that ion-exchanged Pd (isolated Pd) are the Pd species active in NOx storage.

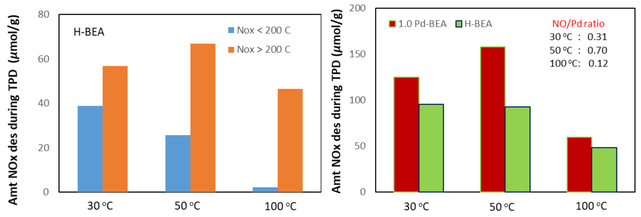
3. Effect of O_2 and H_2O during storage (Si/Al=12.5)



H-BEA: (1) Regardless of NOx feedgas, two distinct NOx release peaks observed in all cases (~100 °C and ~300 °C); (2) NOx feed composition exerted significant impact on NOx release behavior: improved by O_2 but inhibited by H_2O; (3) low-temp. NOx release peak disappeared with H_2O addition, inferring this can be attributed to Brønsted acid sites [2];

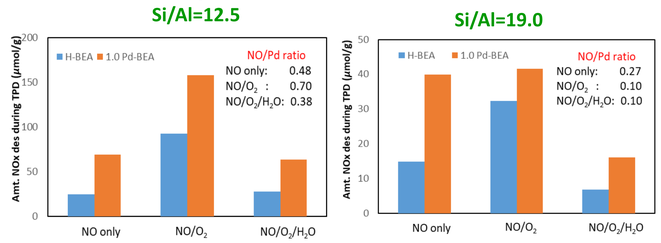
1.0 Pd-BEA: (1) One broad NOx release peak (<300 °C) mainly observed in all cases; (2) similar impact of O_2 and H_2O as on H-BEA; (3) the best NOx desorption performance achieved with O_2 in the feed.

4. Effect of adsorption temperature (Si/Al=12.5)



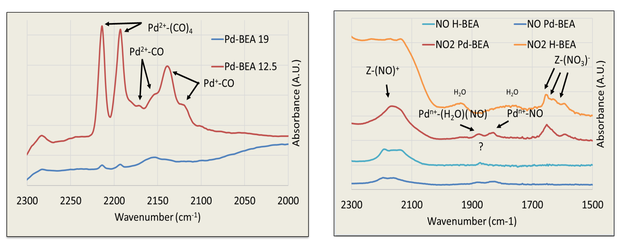
- **H-BEA:** (1) Two distinct NOx release events consistently observed for NOx stored at different temp.; (2) NOx release <200 °C decreased with ads. temp.; NOx release >200 °C relatively unaffected by adsorption temp.
- **1.0 Pd-BEA:** (1) Maximal NOx uptake observed at 50 °C; (2) NO/Pd ratio indicated that Pd achieved the highest utilization for NOx storage at 50 °C.

5. Effect of Si/Al ratio



- Similar NOx-TPD features and impact of O_2 and H_2O observed for Si/Al=19.0 (not shown). However, NOx release ability declined with increased Si/Al ratio in all cases.
- Promotional function of Pd also observed for Si/Al =19.0.
- NO/Pd ratio indicated a higher utilization of Pd for NOx storage with Si/Al=12.5 than 19.0, inferring that utilization of Pd can be tuned by Al content. Increasing Al content can improve NOx adsorption-desorption behavior.

6. DRIFTS study



- **Procedure:** 500 °C in air followed by adsorption of 1000 ppm CO or NO or NO_2 in Ar (10 min) at 25 °C.
- **Si/Al ratio (Left):** CO adsorption shows reduced intensity of Pd^{n+}-CO bands with increased Si/Al ratio, further confirming that isolated Pd is responsible for NOx storage.
- **NO_x adsorption (Right):** (1) NO ads: Z-NO^+ band (H-BEA), Z-NO^+/Pd^{n+}-NO bands (Pd-BEA); (2) NO_2 ads: besides those bands (above), nitrate bands were observed for both, which are likely associated with extra-framework Al (EFAL) sites.

Conclusions

- H-BEA can store significant amounts of NOx in the absence of H_2O, whereas NOx storage in the presence of water is severely depressed.
- H-BEA exhibits two storage sites: Brønsted acid sites (low-temp release) and EFAL (high-temp release).
- Incorporation of Pd into Beta zeolite significantly improved NOx uptake behavior.
- Correlation between NO/Pd and Pd_{iso}/Pd_{tot} implies that isolated (ion-exchanged) Pd is responsible for NOx storage.
- Utilization of Pd for NOx storage (NO/Pd ratio) can be tuned by the Si/Al ratio. Lowering the Si/Al ratio (i.e., increasing the Al content in the zeolite framework) can increase the occurrence of ionic Pd species for NOx storage, and hence improve NOx uptake.
- DRIFTS studies confirmed that ionic Pd is responsible for NOx storage.

Acknowledgements

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References

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[2] H.Y. Chen, J.E. Collier, D. Liu, L. Mantarosie, D. Duran-Martin, V. Novak, R.R. Rajaram, D. Thompselt, Catal. Lett. 146 (2016) 1706.