

Promotion Effect of Water Vapor on co-Adsorption of NO on Pd/Zeolite

Takeshi OHTSU¹, Nao TSUNOJI², Akira ODA¹, Atsushi SATSUMA^{1*} ¹Nagoya University, Department of Materials Chemistry, Furo-cho, Chikusa-ku, Nagoya, Japan. ² Hiroshima University, Department of Applied Chemistry, Kagamiyama 1-4-1, Higashi-hiroshima, Japan. * satsuma@chembio.nagoya-u.ac.jp

Significance and Relevance

It is known that H_2O inhibits low temperature NO adsorption on Pd/zeolite as a Passive NOx Adsorber (PNA). This study discovered that supplying NO and H_2O at 150°C increased the amount of NO adsorbed on Pd/zeolite. The increase in NO adsorption due to H_2O was confirmed in multiple zeolite structures. Observation of the adsorbed species by in-situ FT-IR analysis revealed that the NOx adsorption state changes depending on the NO concentration.

Introduction and Motivations

The selective catalytic reduction (SCR) catalysts are effective for lowering NOx emissions from leanburn diesel engines above 200 °C. However, with the advancement of engine efficiency, NOx reduction at lower temperatures, such as during cold start below 200°C, is strongly required. One of the approaches to suppress NOx emissions at low temperatures is the Passive NOx Adsorber (PNA). The PNA is positioned upstream of the SCR, adsorbs NOx at low temperatures, and releases NOx within the active temperatures of the SCR catalyst. Among various PNA materials, Pd-loaded zeolites are considered the most promising candidates due to their high NOx adsorption efficiency and superior SOx resistance¹. However, challenges remain in preventing the reduction of NOx adsorption capacity due to H_2O adsorption in the exhaust gas². Previous studies have reported that the coexistence of CO enhances NO adsorption even in the presence of H_2O^3 . In this study, we discovered a unique phenomenon that NOx adsorption capacity increases when NO and H_2O were simultaneously supplied to Pd/zeolite.

Materials and Methods

The Pd/zeolite used in this study (Pd/zeolite code - Si/Al ratio) was prepared by loading 1 wt% Pd onto NH₄-type zeolite using the impregnation method, followed by calcination at 600°C for 30 minutes and subsequent steam treatment at 750 °C for 8 hours. The NOx adsorption capacity of the Pd/zeolite was measured by NOx-TPD (temperature-programmed desorption). The NOx-TPD profile was obtained by pre-treating the Pd-zeolite at 600 °C in a 10% O₂/Ar flow for 15 minutes, followed by NOx adsorption at 150 °C by supplying 1020 ppm NO/10% H₂O (if used)/8% O₂/Ar for 1 hour. After that, the sample was purged with Ar for 1 hour to remove physically adsorbed species, and then the temperature increased from 150 to 500 °C at a rate of 5 °C/min under an 8% O₂/Ar flow. To observe NOx adsorption species, in-situ FT-IR spectra were measured using a JASCO FT/IR-6100.

Results and Discussion

Figure 1 shows the NOx adsorption capacity when NO was adsorbed on Pd/zeolites with different structures. In Pd/BEA-13.6, the NOx adsorption capacity decreased when H₂O was introduced during NO adsorption. the in-situ IR results confirmed that no bands attributed to NOx adsorption species were formed on Pd/BEA-13.6 when 1020 ppm NO and 10% H₂O were introduced simultaneously. These results indicate that Pd/BEA-13.6 exhibits a decrease in NOx adsorption capacity due to H₂O, as reported in previous studies⁴. On the other hand, Pd/CHA-13 exhibited an increase in NOx adsorption capacity in the presence of H₂O. This phenomenon has only been reported in a limited number of cases, such as in Pd/FER⁵. Notably, this study revealed that the enhancement of NOx adsorption capacity induced by H₂O is observed not only in Pd/CHA-13 but also across various framework structures. Furthermore, the increase in NO adsorption due to H₂O did not occur unless NO and H₂O were introduced simultaneously to the Pd/zeolite. This suggests that changes in the adsorption state due to the presence of both NO and H₂O influence the NOx adsorption capacity.



Figure 2 shows the NOx adsorption capacity and the in-situ FT-IR spectra during NO adsorption when varying the NO concentration supplied with H_2O on Pd/CHA-13. In Pd/CHA-13, the NOx adsorption capacity increased in the presence of H_2O at any NO concentration. The NOx adsorption capacity varied depending on the concentration of NO adsorbed. The NOx desorption temperature also showed different results depending on the concentration of NO adsorbed. The differences in NOx adsorption and desorption behavior depending on NO concentration indicate that there are distinct NO adsorption states.

The in-situ FT-IR results for NO adsorption on Pd/CHA-13 showed NO-derived bands in the range of 1700–1900 cm⁻¹. When H₂O was absent, bands near 1858 cm⁻¹ and 1810 cm⁻¹ were observed, attributed to Pd²⁺-NO and Pd⁺-NO, respectively⁵⁻⁷. In the absence of H₂O, there was no change in NOx adsorption capacity, and significant changes in adsorption species were not observed. On the other hand, when H₂O was present, bands at 1803 cm⁻¹ and 1750 cm⁻¹ were observed, attributed to Pd²⁺(NO)(H₂O)_x and Pd⁺(NO)(H₂O)_x, respectively⁵⁻⁷. At 500 ppm NO, bands at 1862 cm⁻¹ and 1842 cm⁻¹ were observed, corresponding to Pd²⁺-NO and [Pd(OH)]⁺-NO, respectively^{4,7}, while at 1020 ppm NO, the band at 1803 cm⁻¹ was more dominant. These results suggest that higher NO concentrations allow co-adsorption of NO and H₂O on Pd cations, indicating that NOx adsorption and desorption behavior varies depending on the adsorption state influenced by NO concentration.



Fig.1 (left) NOx desorption amount per catalyst weight of Pd/zeolites calculated from NOx-TPD profiles. NO adsorption conditions: 150°C, 1020 ppm NO, 10% H_2O (if used), 8% O_2/Ar , 50 mL/min (GHSV=20000 h^{-1})

Fig.2 (right) (a) NOx desorption amount of Pd/CHA-13. (b) In-situ FT-IR spectra of NO adsorption state after 30 minutes of NO adsorption. Both of NO adsorption conditions: 150°C, 1020 ppm NO, 10% H₂O, 8% O₂/Ar, 50 mL/min (GHSV=20000 h⁻¹)

References

- 1. H.Y.Chen et al., *Catal Lett.* 146, 1706 (2016).
- 2. A. Porta et al., *Top Catal* **61**, 2021 (2018).
- 3. K. Khivantsev et al., Appl Catal B 280, 119449 (2021).
- 4. Y. Wang et al., Appl Catal A 672, 119605 (2024).
- 5. I. Song et al., Appl Catal B 318, 121810 (2022).
- 6. R. Matarrese et al., Appl Catal B 331, 122723 (2023).
- 7. Y. Liu et al., ACS Omega 9, 30452 (2024).

Acknowledgments

This work is based on the results of JPNP14004, a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO) and entrusted to The Research Association of Automotive Internal Combustion Engines (AICE).