Pd based passive NO_x adsorbers for low temperature emission control

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Highlights

- Small pore zeolite (Pd/SSZ-13) results in larger NO_x desorption above 200ºC
- Addition of CO beneficial for NO storage, especially for small pore Pd/zeolites
- Pd ions critical for good PNA, especially when CO is present
- Ceria addition to Pd/zeolites is beneficial when CO is not present

1. Introduction

Urea SCR is a powerful technique for removing NO_x from vehicle exhausts. However, urea dosing can only be done from about 200°C, because at low temperature the urea will form deposits. An interesting new concept is to use PNA [1-2] upstream of the SCR catalyst. The role of the PNA is to adsorb NO_x at low temperature, where urea cannot be dosed and at higher temperature, thermally release the NO_x. It is critical that the release temperature is above the temperature for urea dosing, but at the same time not too high so that the NO_x can be released in normal conditions. We have earlier examined Ag/Al_2O_3 as an PNA[1] and, $Pd/Ce/Al_2O_3$ [2] and Pd/zeolites [3] have also been studied as PNA. However, materials for PNA catalysts needs further development in order to find a catalyst that release NO_x in the optimum temperature interval. The objective of the current work is to examine different Pd/zeolites and also the effect of incorporating ceria in order to enhance storage in the optimal temperature window. To our knowledge, the effect of combining Pd/zeolites with ceria for PNA applications has not been shown in any journal publications.

2. Methods

Several Pd based catalysts were synthesized, using BEA with two silica to alumina (SAR) ration and SSZ-13 also with two SAR. All catalysts contained 1% Pd. In addition, the effect of adding 5 or 10% ceria to the catalysts was studied. Finally, $Pd/Ce/Al_2O_3$ was prepared as a base catalyst to compare the other results with. The catalyst powders were coated on monoliths (2 cm in lengths and 2 cm in diameter). The passive NO_x storage was examined in a flow reactor equipped with an FTIR using temperature programmed desorption (TPD) technique. The catalyst was exposed to 200ppm NO+8% O_2 for 30 min at 80°C, followed by flushing with 8% O_2 for 15 min and finally increasing the temperature to 400°C with a rate of 20 °C/min. This experiment was repeated four times, with the introduction of 5% H_2O, 5%CO_2+5% H_2O or 400ppm CO+5%CO_2+5% H_2O.

3. Results and discussion

Pd/SSZ-13 and Pd/BEA catalysts with different SAR ratios was studied for passive NO_x adsorption and compared with a $Pd/Ce/Al_2O_3$ catalyst. Small pore zeolite (Pd/SSZ-13) resulted in larger NO_x desorption at temperatures above 200ºC compared to large pore zeolite (Pd/BEA), which can be seen in Figure 1. According to Vu et al. [3], the addition of CO is beneficial for NO_x storage over Pd/BEA. Interestingly, we find that the beneficial effect is significantly larger for the small pore Pd/SSZ-13 (see Fig. 1). DRIFT results showed the palladium was in ionic form for the palladium zeolites (bands around 1800 cm^{-1}, see Fig. 2), thus it is critical to have palladium ions to receive the high temperature desorption. Moreover, when adsorbing NO on Pd zeolites, water must desorb, which is seen by the negative bands around 2500-3800 cm^{-1}. This is not the case for $Pd/Ce/Al_2O_3$ and we suggest that the reason for this is sterical restrictions, in combination with large water storage in the zeolites. When the Si/Al ratio is higher (compare Pd/SSZ-13 (SAR~13), Fig. 2b with Pd/SSZ-13 (SAR~6), Fig. 2a) the removal of hydroxyl groups is larger. The reason for this is that for high Si/Al ratio more Pd binds to one Al and charge balanced with an OH-group (instead of binding to two

Al), since there are less Al sites available. Thus, there is more OH that needs to be removed in order to store NO. Another interesting effect is that bands for interactions with the nitrosyls with the Pd and support is found for the Pd/Zeolites (ca 2200-2300 cm^{-1}), which was not the case for Pd/Ce/Al_2O_3. In addition, the effect of ceria addition to the catalyst was studied and it was found that the ceria addition resulted in more NO_x desorbing at higher temperature for the Pd/BEA and that the storage temperature could be shifted to lower temperature for Pd/SSZ-13. However, the ceria addition resulted in lower amounts of ionic palladium and this might be a reason for different effects when adding CO during the storage.

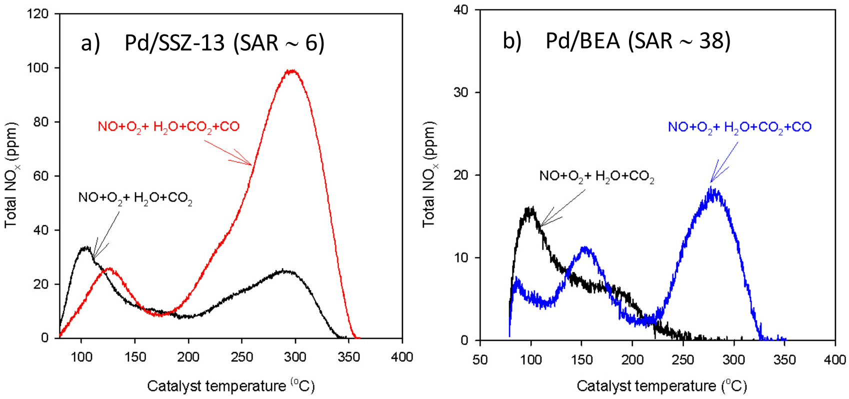

Figure 1. NO_x desorbed after NO storage at 80 °C using $NO+O_2+H_2O+CO_2$ or $NO+O_2+H_2O+CO_2+CO$ for a) Pd/SSZ-13 (SAR ~ 6) and b) Pd/BEA (SAR ~ 38).

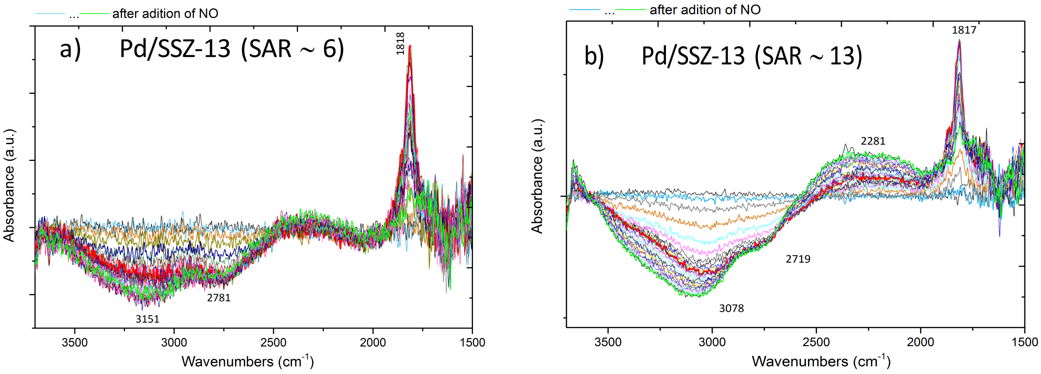

Figure 2. DRIFT results for NO storage at 80 °C in the presence of O_2 and H_2O for Pd/SSZ-13 with a) SAR ~ 6 and b) SAR ~ 13.

4. Conclusions

Pd/SSZ-13, Pd/BEA, Pd/Ce/Al_2O_3, Pd/Ce/BEA and Pd/Ce/SSZ-13 was studied for passive NO_x adsorption using TPD experiments in various gas mixtures. In addition, in order to understand the mechanisms for the different surface reactions, in-situ DRIFT spectroscopy was used. We found that small pore zeolites release more NO_x at higher temperature and that the NO_x release characteristics was dependent both on zeolite structure and Si/Al ratio. Ionic palladium was observed for the palladium zeolites, which was not the case for the Pd/Ce/Al_2O_3 sample, and this could be one reason the high temperature release. The addition of ceria was beneficial for the NO_x release, especially for Pd/BEA that received more NO_x that had a higher stability. Finally, the addition of CO during storage was beneficial for Pd/BEA, but significantly more for Pd/SSZ-13.

References

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Keywords
Passive NOx adsorbers, PNA, palladium, zeolites.