The effect of ceria on palladium based passive NOx adsorbers

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Abstract: Passive NO_x adsorbers (PNA), studied here, is a concept for removing NOx at low temperatures from vehicle exhaust. They should store NO_x at low temperature where selective catalytic reduction (SCR) catalyst is not working, and thermally release the NO_x at high temperature. In this work the effect of Ce addition on Pd/BEA efficiency for NO_x storage was investigated and compared to Pd/Ce/Al_2O_3. NO_x release characteristics was dependent both on zeolite structure, Si/Al ratio and Ce addition. In-situ DRIFT studies showed that ionic palladium species are critical. Moreover, addition of ceria to Pd/BEA increased the stability of the NO_x species, which is very beneficial.

Keywords: Passive NOx adsorbers, palladium, zeolites.

1. Introduction

Demand for lower NO_x emissions parallel with the need for efficient vehicles is shifting the exhaust temperatures towards lower values but the problem is lack of catalyst activity at low temperatures[1]. For instance urea selective catalytic reduction (SCR) is highly effective for removing the NO_x but due to tendency to form deposits[2] in the after-treatment system at low temperatures, urea cannot be dosed until 180-200°C. There is therefore a need for catalyst that can remove NO_x at temperatures below 200°C and this is becoming imperative for a sustainable future. A possible solution to the mentioned problems is the use of Passive NO_x adsorbers (PNA). These materials should adsorb NO_x at low temperature and release the NO_x thermally at temperatures above 200°C, where urea can be dosed and the SCR system works efficiently.

2. Experimental

Several Pd based catalysts were synthesized, using BEA with two silica to alumina (SAR) ratio. 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. Better understanding of crystal structure effect on activity was done through XRD studies. Moreover, DRIFT spectroscopy was used for retrieving a fundamental understanding of the surface reactions. In these experiments after pretreatment at 550°C with 8% O_2 and 1% H_2O for 30 min, the background was taken at 80 °C in a presence of 8% O_2, and 1% H_2O and afterwards spectra were recorded with the addition of 1000ppm NO.

3. Results and discussion

The effect of adding ceria to the Pd/BEA catalysts with different SAR ratios was studied for passive NO_x adsorption using NO TPD and the resulting NOx concentrations during the thermal desorption are presented in Figure 1. On the left panel are results for SAR = 38 and on the right for SAR = 300. As it can be seen, even without adding Ce, the profile for Pd/BEA is different for different SAR values, where lower SAR (38) have the main desorption peak at 100°C compare to SAR(300) desorption peak around 180°C. When Ce was added to Pd/BEA two NOx desorption peaks are noticed with the dominant peaks shifted for both samples above 200°C. This is very beneficial since urea dosing for the SCR system can be done from 200°C. It should be mentioned that for Pd/Ce/Al_2O_3 desorption peak is located around 180°C, thus the high stability of the NOx for Pd/Ce/BEA is due to interactions between the zeolite, palladium and ceria. In order to better understand the results from surface interaction point, DRIFT spectroscopy was used and the results for Pd/BEA(38) and Pd/10%Ce/BEA(38) are shown in Figure 2. The palladium is in ionic form, detected around 1800 cm^{-1}, in the Pd/BEA. Interestingly, the addition of ceria results in a shift of this band to 1726 cm-1 and this peak is not visible for Pd/Ce/Al_2O_3. This results clearly show that there is an interaction between ceria, palladium and the zeolite during the NO adsorption. Moreover, for the Pd/Ce/BEA sample surface nitrates are found at 1541cm^{-1}, which can be assigned to NO binding to the Pd/Ce sites.

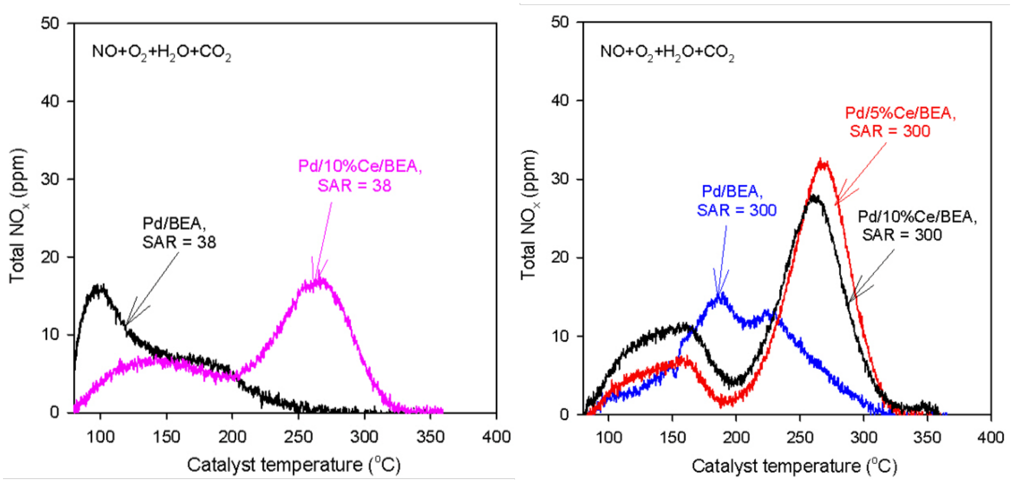

Figure 1. NO_x desorbed after NO storage at 80 °C using $NO+O_2+H_2O+CO_2$ for Pd/BEA(SAR=38) (with and without 10%Ce, left figure) and Pd/BEA(SAR=300) (without and with 5%,10%Ce, right figure).

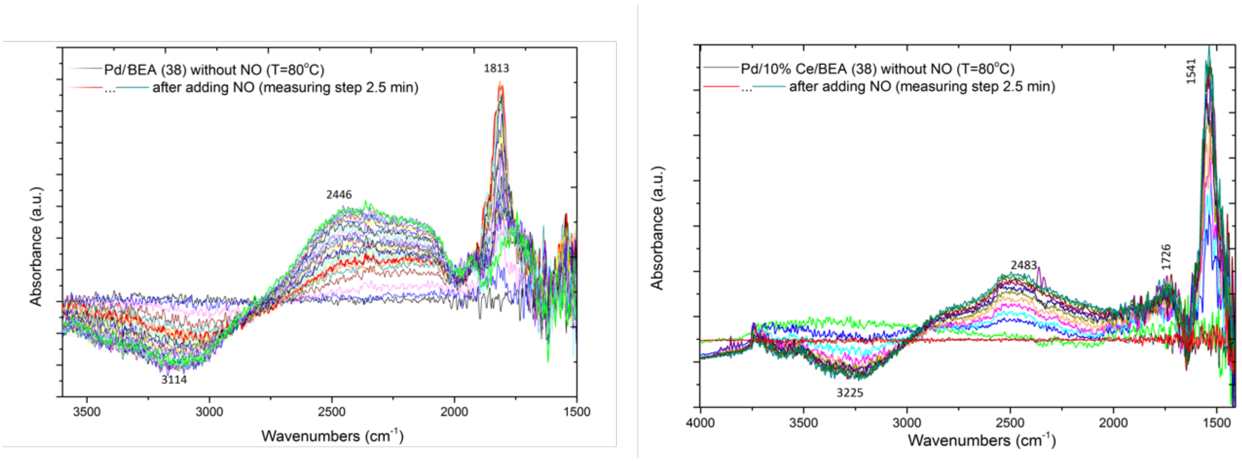

Figure 2. DRIFT results for NO storage at 80 °C in the presence of O_2 and H_2O for Pd/BEA(38) without Ce (left figure) and with 10%Ce (right figure).

4. Conclusions

Using TPD experiments in various gas mixtures Pd/BEA, Pd/Ce/Al_2O_3, Pd/Ce/BEA was studied for passive NO_x adsorption. In-situ DRIFT was used for better understanding of surface reaction mechanisms. NO_x release characteristics was dependent both on zeolite structure, Si/Al ratio and ceria addition. The ceria introduction resulted in more stable NOx species, which is beneficial for the PNA concept.

References

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