Operando FT-IR spectroscopy analysis of NOx adsorption/desorption over Pd-doped zeolites: Effect of temperature, water and oxygen on NOx uptake and release

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Highlights

- Catalyst characterization indicates the presence of isolated Pd species (with oxidation states +1 and +2) and (minor) PdO particles.
- H_2O exhibits strong stabilizing effect on the thermal stability of adsorbed species, and slightly modifies the NO storage capacity.
- Oxygen has a minor effect on the catalyst adsorption capacity and on the stability of the nitrosyls.

1. Introduction

Significant amounts of NOx are emitted during vehicle cold-start, since after-treatment devices like SCR and/or LNT systems are inactive at low temperature [1,2]. A possible solution is the adoption of low temperature NOx adsorbers, the so-called Passive NOx Adsorbers (PNAs) that utilize their ability to temporarily store NOx at low temperature (<150 °C) and release at higher temperature. The use of Pd-promoted zeolites has been suggested, which however must be optimized in view of the high cost of the active Pd component. Goal of this study is to deepen mechanistic aspects related to the low-T adsorption/desorption of NOx and to envisage by means of Operando FT- IR Spectroscopy and microreactor studies the role of species like O_2 and H_2O and adsorption temperatures on the performance of catalyst.

2. Methods

An home-made Pd-doped chabazite sample (Pd_1/SSZ-13, Pd loading 1% w/w) calcined at 750°C has been investigated in this study. The Pd_1/SSZ sample was prepared by impregnation of the zeolite support in excess of solvent using aqueous $Pd(NO_3)_2$ solution; a sample prepared by ion exchange (Pd loading 0,3% w/w has also been prepared). Standard NOx adsorption experiments were conducted both in a microreactor apparatus and in an operando FT-IR cell (#CSX, AABSPEC) at different adsorption temperatures (80°C, 120°C and 150°C). The thermal stability of the NOx stored species has been investigated by temperature programmed desorption (TPD) and the experiments have been done in the presence/absence of H_2O and O_2 [3].

3. Results and discussion

The catalyst characterization carried out by in-situ CO/NO adsorptions and FT-IR spectroscopy, shows on both samples the presence of isolated Pd^+ and Pd^{2+} species, formed by ion exchange with the Brønsted acid sites of the zeolite, and of PdOx particles (mainly on the impregnated sample) on the external surface of the zeolite. Upon addition of NO/O_2 mixture over the impregnated sample in the presence of water and oxygen (standard run) (see data at 150°C in Fig. 1), the NOx (NO + NO_2) concentration increases with time reaching slowly the inlet concentration value (300 ppm) indicating the capacity of the catalyst to trap NO. During NO adsorption, the formation of Pd^{n+} nitrosyls in the form of anhydrous or hydrated complexes involving Pd^{2+} to Pd^+ sites are observed in the range 1800-1860 cm^{-1} depending on the adsorption temperature. The NO adsorption is accompanied by NO_2 evolution due to the reduction of Pd^{2+} to Pd^+ sites (see Fig. 1A). The absence of water (Fig. 1B) has a huge effect on the results, in that the stability of adsorbed surface species decreases due to the prevalence of Pd^{2+} nitrosyls that have lower stability, thereby shifting NO desorption to occur towards low-Temperature region i.e. < 220°C

(Fig.1B). In the absence of water, also the NO_2 formation is different, in that the initial Pd^{2+} to Pd^{+} reduction by NO is not observed while the catalytic NO to NO_2 oxidation is evident at the end of adsorption. This indicates that water favors the reduction of the Pd^{2+} species by NO.

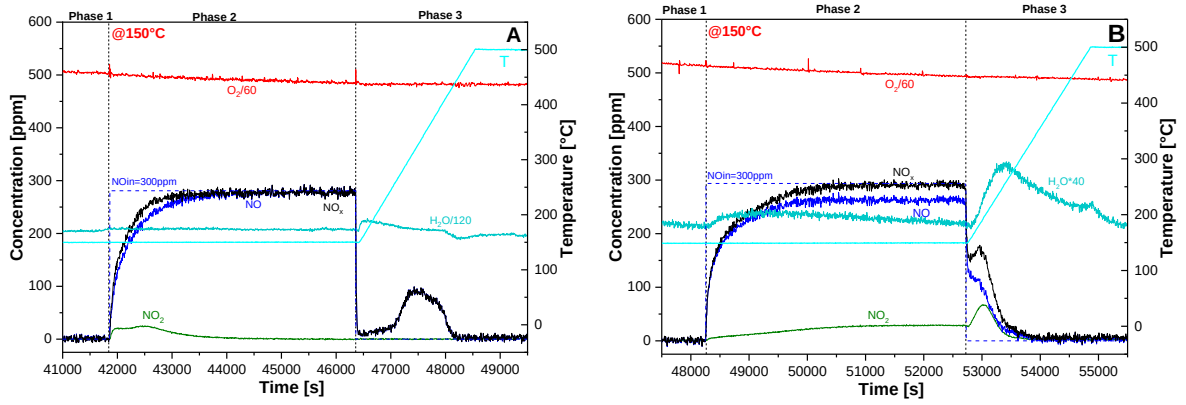

Figure 1. Gas phase NO adsorption (phase 2) and subsequent TPD (phase 3) runs over impregnated Pd/SSZ-13 at 150°C in presence of: (A) water and oxygen; (B) only oxygen.

Oxygen on the other hand has no effect on NO adsorption (data not shown) but its presence tends to decrease the stability of the adsorbed nitrosyls, due to the reoxidation of Pd^{+} to Pd^{2+} and to the lower stability of Pd^{2+} nitrosyls. The effect of different adsorption temperatures (80°C, 120°C and 150°C) showed similar nitrosyls formation at all investigated temperatures, with an additional formation of nitrates at the lowest investigated temperatures.

Notably, very similar results have been obtained over both the impregnated and ion-exchanged catalysts.

4. Conclusions

In this work, mechanistic aspects of NO adsorption/desorption over home-made Pd/SSZ-13 PNA materials have been examined through NOx adsorption and desorption experiments conducted in a micro-reactor and operando FT-IR apparatus. The effects on the NO adsorption/desorption characteristics due to the presence of H_2O and O_2 at various adsorption temperatures (80°C, 120°C and 150°C) have been investigated. Upon NO adsorption, the observation of Pd^{n+} nitrosyls are noted, forming anhydrous and hydrated complexes that encompass Pd^{2+} to Pd^{+} sites within the 1800-1860 cm^{-1} range. The experimental findings demonstrate the excellent capacity of Pd doped chabazite to adsorb NO. Water has a significant impact in that its absence has a strong destabilizing effect over the NO_x adsorbed species. In contrast, oxygen has no impact on NO adsorption and slightly decreases the stability of the adsorbed nitrosyls.

References

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Keywords
Pd-doped zeolites, NOx adsorbers, PNA, SSZ-13, Operando FT – IR Spectroscopy.