

Isotopic studies of NO_x reduction over Pt-Ba/Al₂O₃ LNT catalyst

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Introduction

NO_x storage and reduction (NSR) catalysts (or lean NO_x trap, LNT) are considered to be one of the most promising solutions for NO_x removal from lean burn engine exhausts [1]. In a recent study by some of us [2], a mechanism for the reduction by H₂ of NO_x stored onto a Pt-Ba/Al₂O₃ LNT model catalyst has been proposed. In particular it has been suggested that the formation of N₂ occurs via a 2-steps in series molecular pathway involving at first the formation of NH₃ upon reaction of stored NO_x with H₂ (step 1), followed by the reaction of NH₃ with residual stored NO_x to give N₂ (step 2). It has also been found that step 1 is faster than step 2, which is rate determining in the formation of N₂.

The present study aims to better elucidate the pathways involved in the reduction of the stored NO_x, and in particular the second step of the proposed mechanism for N₂ formation involving stored NO_x and ammonia. For this purpose experiments have been carried out using isotopically labelled molecules and different reductants, including H₂ and NH₃.

Materials and Methods

Mechanistic aspects in the reduction of stored NO_x has been investigated using NH₃ (1000 ppm) and H₂ (2000 ppm) as reductants under both isothermal conditions and temperature programming (Temperature Programming Surface Reaction, TPSR). NO_x have been stored on a model Pt-Ba/Al₂O₃ catalyst at different temperatures, feeding either NO or isotopically labelled ¹⁵NO (1000ppm) in O₂ (3%) + He. The reduction products were monitored with an UV-Vis analyzer (LIMAS H11, ABB) and a mass-spectrometer (Thermostar, Pfeiffer Vacuum) in order to quantify all the isotopic species present at the reactor outlet.

Results and Discussion

The reactivity of the reductants with adsorbed NO_x (i.e. nitrite and nitrate) species has been investigated. These species are obtained upon NO_x adsorption at low and high temperature, respectively [3]; notably, nitrites has been claimed as intermediate in the reduction of the stored nitrates.

Fig. 1 shows the results of the TPSR run using ¹⁴NH₃ as reductant after ¹⁵NO adsorption at 150°C in the presence of oxygen. Due to the low adsorption temperature, nitrite formation is expected upon storage. Accordingly the following overall stoichiometry of reduction is the expected: $\text{Ba}(\text{NO}_2)_2 + 2 \text{NH}_3 \rightarrow 2 \text{N}_2 + \text{BaO} + 3 \text{H}_2\text{O}$ (1) i.e. N₂ formation involves equimolecular amounts of nitrites and NH₃ (in fact the formal oxidation state of N in the nitrite and NH₃ is +3 and -3, respectively).

As apparent from the Figure, the NH₃ concentration initially increases due to its desorption and then decrease being consumed in the reaction with stored NO_x. The temperature threshold for the reaction can be set near 150°C where the evolution of the reduction products is observed. Only nitrogen has been observed, with different isotopic composition. Notably, the

NH₃ consumption and N₂ formation is very close to that of reaction (1), although a slight higher NH₃ consumption is observed. This might suggest the presence of traces of nitrates on the surface together with nitrites, as also pointed out by the N isotopic distribution (see below) showing that the overall amount of ¹⁴N atoms in the products is slightly higher than that of ¹⁵N atoms.

Concerning the N₂ isotopic distribution in the products, ¹⁵N¹⁴N (m/z = 29) represents the main product, along with minor amounts of ¹⁴N₂ (m/z = 28) and ¹⁵N₂ (m/z = 30). Based on this distribution, the preferential route for the formation of N₂ is the coupling of one N atom coming from the nitrite (¹⁵NO₂) and the other from ¹⁴NH₃. This pathway may have same analogies with N₂ formation in the NH₃-SCR reaction, where the formation of intermediate surface species (i.e. nitrosamide and/or ammonium nitrite) formed upon coupling of one N atom from gaseous NO and one N atom from NH₃ has been claimed [4]. However, the presence of non negligible amounts of other N₂ products (i.e. ¹⁴N¹⁴N and ¹⁵N¹⁵N) indicates that N₂ is also formed upon coupling of two N atoms coming from the stored nitrites (¹⁵N¹⁵N) and from ammonia (¹⁴N¹⁴N). Accordingly other reduction route should be considered, e.g. decomposition of nitrite and NH₃ on Pt sites with formation of Pt-N adatoms followed by recombination to N₂. Further experiments are under way to investigate these preliminary findings and to clarify the pathways involved in the reduction of the stored NO_x.

Significance

New insights in the pathways involved in the reduction of the stored NO_x are here provided by using transient methods and isotopic labeled molecules.

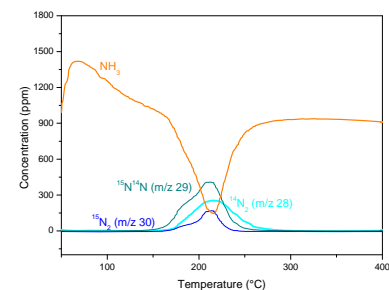


Figure 1. TPSR experiment in NH₃ after ¹⁵NO/O₂ storage at 150°C over Pt-Ba/Al₂O₃ catalyst.

References

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