

Study of the reduction by H₂, CO and NH₃ of NO_x species stored over Pt-Ba/Al₂O₃ Lean NO_x Trap systems

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Introduction

In order to reduce NO_x to N₂ under oxygen-rich environment with acceptable fuel efficiency loss in the '90s the Toyota researchers proposed the so-called NSR catalysts (NO_x Storage-Reduction concept) [1]. In spite of the fact that these catalysts are being used at commercial scale in Japan, a common agreement on the mechanistic aspects of the storage of NO_x species and of their reduction is still lacking [2]. In this paper the reduction of NO_x adsorbed species is studied using different reducing agent, namely hydrogen and CO. Besides, as ammonia is known to be by-product of the regeneration procedures, herein we investigate its possible involvement in the reduction mechanism.

Materials and Methods

The study was performed over an homemade Pt-Ba/γ-Al₂O₃ (1/20/100 w/w) ternary catalyst: the was prepared by incipient wetness impregnation of commercial alumina with aqueous solution of dinitro-diammine platinum and subsequent of barium acetate, dried overnight at 80°C in air and calcined at 500°C for 5 h.

The NO_x reduction capability of the various reductants was investigated in the range 200-350°C by transient experiments performed in a flow micro-reactor system equipped with a mass spectrometer for product analysis. NO_x were always adsorbed at 350°C starting from NO (1000 ppm) in 3% v/v O₂; the stored NO_x were then reduced at different temperatures, in the range 100-350°C, by admission of several pulses of the reductant.

Results and Discussion

A typical reduction carried out at 350°C with H₂ as reducing agent is presented in Figure 1. In the initial pulses, H₂ is completely consumed and the stored NO_x are reduced selectively to N₂. After few cycles, hydrogen appears into the gas phase: simultaneously the concentration of nitrogen decreases slowly, and evolution of ammonia is detected. The same experiment performed at lower temperatures (300, 250, 200°C) shows that progressively the regeneration procedures become less efficient, that is a not complete removal of the stored NO_x is achieved, as apparent from data showed in Figure 2.

When CO was used reducing agent ammonia is never detected among the reduction products. Nevertheless, even at the highest investigated temperature, CO is less efficient than hydrogen in removing the NO_x adsorbed species (figure 2). Dedicated investigations concerning the study of the reactivity of CO over LNT systems suggested that CO may adsorb onto Pt sites, blocking their activity towards the reduction of NO_x species.

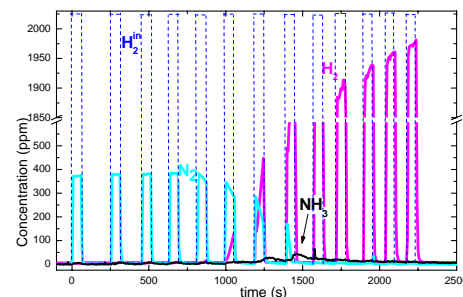


Figure 1 – Lean-rich cycles at 350°C with hydrogen.

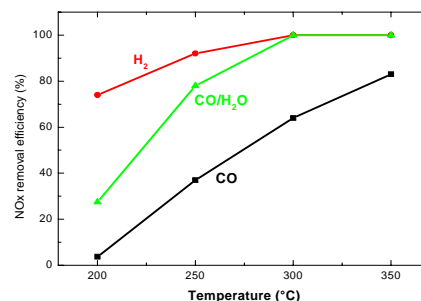


Figure 2 – NO_x removal efficiency as a function of T during reduction with H₂, CO, CO+H₂O

The reduction with CO was also studied in the presence of 1%v/v water in the feed flow. Inspection of Figure 2 points out that water enhances the reactivity of CO: indeed at 300 and 350°C the NO_x removal efficiency is complete and equal to that measured when hydrogen is used. It is suggested that reduction of the stored NO_x by CO may involve the preliminary formation of hydrogen according to the water gas shift reaction.

Finally, ammonia was

tested as reducing agent: in facts, it is known [2,3,4] that ammonia is the most important by-product in LNT regenerations by hydrogen. A specific study was undertaken to understand if ammonia might be involved in N₂ formation according to an in-situ SCR mechanism. The results showed that ammonia is able to reduce nitrates very efficiently already at low T and that complete selectivity to nitrogen is always achieved. Thus its possible involvement as intermediate species in the mechanism governing the reduction of NO_x adsorbed specie by H₂ over LNT catalyst can not be ruled out.

Significance

LNT systems are becoming the first choice for the abatement of NO_x species from the exhausts of light vehicles. The understanding of the mechanisms that determine the chemistry of both the lean and the reduction phases are thus mandatory for an optimization of the catalytic performances as well as for the development of detailed kinetic schemes that allows mathematical modeling of real converters.

References

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