

Selectivity aspects of the reduction of stored NO_x over Pt-Ba/Al₂O₃ Lean NO_x Trap systems

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Introduction

The so-called Lean NO_x Traps (LNT) represent a viable solution for the abatement of NO_x emissions from lean-burn engines [1]. These systems (e.g. Pt-Ba/Al₂O₃) work under periodic changes between lean (NO_x storage) and rich conditions (NO_x reduction). Several studies were published on the mechanisms of both the NO_x storage [1,2] and reduction [1,3] steps, but a complete understanding of these processes is still lacking. In particular, concerning the reduction phase, a detailed comprehension of the process, of the role of the different reducing agents and of the possible pathways originating the various products (i.e. NO, N₂O, nitrogen, ammonia) is still lacking. These are however crucial aspects of the reaction in the light of controlling the selectivity of the reduction process.

In previous studies [3] we showed that on Pt-Ba/Al₂O₃ catalyst the reduction process is not initiated by the thermal decomposition of the stored NO_x ad-species, but a catalytic pathway involving Pt is instead operating. In this study new data are presented that extend and complete the picture of the mechanism of the reduction process by hydrogen: the effect of the presence of CO₂ and/or of water in the feed flow was investigated in a wide T-range, in particular addressing the selectivity of the reduction process.

Materials and Methods

An homemade Pt-Ba/γ-Al₂O₃ (1/20/100 w/w) sample was employed in this study and 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.

NO_x were always adsorbed at 350°C by imposing a rectangular step feed of NO (1000 ppm) in flowing He + 3% v/v O₂; the stored NO_x were then reduced at different temperatures, in the range 100-350°C, by imposing a stepwise change in the H₂ concentration (2000 ppm). The effect of the presence of water (1% v/v), CO₂ (3000 ppm) and H₂O (1% v/v) + CO₂ (3000 ppm) during the regeneration phase was also analysed.

Results and Discussion

The admission of H₂ at 350°C on the catalyst following NO/O₂ adsorption at the same T results in the complete consumption of the reductant, and in the immediate selective formation of N₂. Small amounts of NO are detected in the gas phase at the beginning of the reduction process. Then, hydrogen appears into the gas phase and the concentration of nitrogen decreases; after H₂ breakthrough, evolution of ammonia is observed. No N₂O formation was observed.

Notably, the selectivity of the process is affected by the initial NO_x loading: in facts, ammonia formation increases upon increasing the NO_x coverage.

The effect of temperature on regeneration procedures was then addressed by performing the reduction processes at various temperatures, in the range 150-300°C, after NO_x adsorption at 350°C. Upon decreasing the reduction temperature, a higher ammonia formation is observed, along with a not complete removal of the stored NO_x (Figure 1).

The presence of water in the feed flow was investigated performing the reduction of NO_x stored at 350°C in the presence of H₂O: it was found that water favored the NO_x reduction at low T, allowing a better regeneration of the catalyst. No significant effects on the nitrogen selectivity were observed. As opposite, when CO₂ was added to the hydrogen flow the reactivity of the system was inhibited and ammonia was the main product in the whole investigated range of temperatures (Figure 1).

On the basis of these data, a reaction pathway involving the NO_x release upon H₂ admission followed by NO_x reduction over Pt can be envisaged, in which the selectivity of the process is governed by the local NO_x/H₂ ratio on Pt. Water favors the process by enhancing the H₂ spillover, whereas CO₂ inhibits the reaction being reduced to CO which blocks the Pt sites.

Significance

The detailed knowledge of the catalytic behavior of the "NO_x storage/reduction" systems and in particular the comprehension of the parameters that determine the selectivity of the reduction process are key factors in the optimization of the operating conditions and in the rationalization of the catalyst formulation of LNT systems.

References

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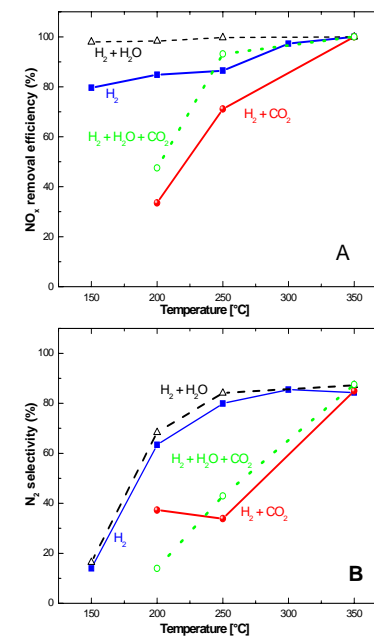


Figure 1 – NO_x removal efficiency (A) and N₂ selectivity (B) as a function of T during reduction with H₂, H₂+H₂O, H₂+CO₂, H₂+H₂O+CO₂