

Identifying critical factors in the regeneration of NO_x-trap materials under realistic conditions using fast transient techniques coupled with isotopically labelled ¹⁵NO

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Introduction

NO_x Storage and Reduction (NSR) catalysts are one of the most promising solutions to meet forthcoming NO_x exhaust emission regulations. Much research has been carried out in this area in the decade since Takahashi et al. [1] introduced the NO_x storage concept. However, despite the high level of activity in this area, it is surprising that most studies have been conducted under conditions that are far from realistic conditions. In the present work a fast transient apparatus has been developed to study NSR catalysts under realistic temporal conditions, *i.e.* where the storage time was 1 - 2 minutes and the regenerative rich time was of the order of 1 - 2 s [2]. The performance of 1%Pt/17.5%Ba/γ-Al₂O₃ NSR catalyst was studied as a function of the temperature, rich phase duration, reductant concentration, the type of reductant and the effect of an inert gas purge. The results of this study highlighted the importance of the regeneration step in the NO_x storage performance, leading us to also investigate the role of Rh in the NSR mechanism using isotopically labelled ¹⁵NO as a feed. The combination of fast transient kinetics and isotopically labelled ¹⁵NO has allowed us to gain a unique insight into the behaviour of these traps.

Materials and Methods

The 1%Pt/17.5%Ba/γ-Al₂O₃ (Pt-NSR) and 1%Pt/0.7%Rh/17.5%Ba/γ-Al₂O₃ (PtRh-NSR) catalysts were prepared by wet impregnation of a commercial γ-Al₂O₃. The catalyst was tested in a system specially designed to allow fast switching between gas streams. This consisted of a series of flow controllers feeding gases to VICI helium actuated low volume switching valves connected to a 3mm i.d. quartz plug flow reactor. Analysis of the products and reactants was by means of a Hiden HPR 20 quadrupole mass spectrometer. The overall time resolution of the switch (including valve switching, purge time and analysis) was 150 ms. The use of ¹⁵NO as a feed allowed the products ¹⁵N₂, ¹⁵NO₂, ¹⁵N₂O to be monitored under conditions where the products of ¹⁴NO would normally overlap with fragments of CO₂ and CO.

Results and Discussion

The results of this study show that for the Pt-NSR catalyst at low regeneration times (1.2 s) typical of those found in real NSR systems, the NO_x storage performance deteriorated from cycle to cycle. The inefficiency in the performance can be explained by an insufficient rate of reduction of the released NO_x. Experiments in which a purge phase (containing CO₂ and H₂O) was introduced after the rich pulse showed that significant quantities of NO_x were released during the purge phase. The released NO_x does not reabsorb during the purge because of the lack of oxygen required to form nitrate species. However, under normal operating conditions, where the rich phase is followed immediately by the lean phase, some of the NO_x

released during the rich phase may react with oxygen at the interface of the lean/rich phase to re-form stable nitrate species, thus resulting in only partial regeneration of the trap.

The PtRh-NSR trap is better at reducing the stored NO_x to N₂, the data in Figure 1 shows that it exhibits unusual behaviour during regeneration. During the course of the 2 s regeneration phase there are two ¹⁵N₂ release events, the first one corresponds to the point at which the switch from lean to rich occurs and the second from rich to lean, in between these two spikes there is no production of any N-containing products. We speculate that the second release of ¹⁵N₂ can be attributed to selective oxidation of ¹⁵NH₃ stored on the catalyst.

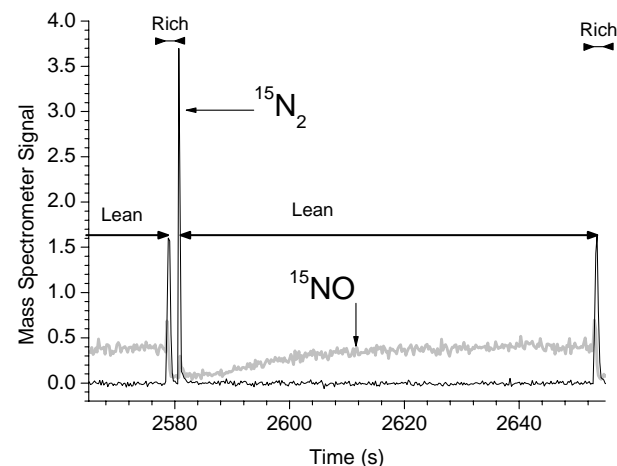


Figure 1: Evolution of mass spectrometer signal during NSR reaction over PtRh-NSR at 300°C. Feed Conditions: Lean (72 s): 10% H₂O, 10% CO₂, 5% O₂, 300ppm ¹⁵NO, bal Ar + Kr. Rich (2 s): 10% H₂O, 10% CO₂, 4.5% CO, 1.5% H₂, bal. Ar.

Significance

The combination of fast transient kinetics and use of isotopically labelled ¹⁵NO to study the NSR reaction is unique. It provides an invaluable method of studying the performance of Pt and Pt/Rh NSR traps under *realistic* conditions. In particular, it gives an insight into the crucial regeneration step of the NSR reaction which typically occurs in ~ 1 s.

References

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2. J.P. Breen, C. Rioche, R. Burch, C. Hardacre, F.C. Meunier, Appl. Catal. B, 72 (2006) 178.