

Isotopic Studies of NO_x Storage and Reduction over Pt/BaO/Al₂O₃ using Temporal Analysis of Products

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Introduction

NO_x Storage and Reduction (NSR) is an emerging technology for NO_x emission abatement in lean burn gasoline and diesel engines. The NO_x removal process involves storage of NO_x on an alkali earth component (Ba, Ca) mediated by precious metals (Pt, Rh) followed by injection of a rich pulse for a shorter duration to reduce the stored NO_x. In this study, we employ Temporal Analysis of Products (TAP) experiments with isotopic labeling to elucidate the regeneration chemistry. TAP experiments are carried out isothermally in the Knudsen transport regime, thereby avoiding thermal and mass transport complications typical of atmospheric pressure reactors. TAP experiments are carried out utilizing isotopic species on Pt/BaO/Al₂O₃ catalysts with varied Pt loadings and dispersions but an equal number of exposed Pt sites. The use of labeled ¹⁸O₂ and ¹⁵NO provided resolution of reaction pathways such as for N₂ formation during the regeneration step. The experiments help to elucidate the roles of Pt and the coupling between the precious metal and storage phases. .

Materials and Methods

Two Pt/BaO/Al₂O₃ powder catalysts were used having vastly different Pt loading (wt.%) and dispersion, but equal exposed Pt sites (catalysts provided by BASF Inc.; Table 1). While sample D3 was used as provided, sample B2M was a physical mixture of Pt/BaO/Al₂O₃ and BaO/Al₂O₃, the latter of which was added to achieve the requisite BaO sites. The TAP studies involved feeding pulses of the reactant over catalysts over 150°C - 400°C. The feed gas consisted of NO, H₂, ¹⁵NO (98 atom% ¹⁵N, Cambridge Isotope Laboratories) and ¹⁸O₂ (99 atom% ¹⁸O, Icon Isotopes). The use of labeled ¹⁵NO enabled the probing of pathways to the N-containing products. Effluent species included H₂ (m/e=2), N₂ (m/e=28), ¹⁵NN (m/e=29), ¹⁵N₂ (m/e=30), NO (m/e=30), ¹⁵NO (m/e=31), O₂ (m/e=32), ¹⁵N¹⁸O (m/e=33), ¹⁸OO (m/e=34), ¹⁸O₂ (m/e=36), and N₂O (m/e=44) and were monitored with a quadrupole mass spectrometer. Two kinds of experiments are performed: (i) pulse storage experiments, in which NO (or ¹⁵NO) was pulsed with a spacing time of τ_s, and (ii) pump-probe NSR experiments in which sequential pulses of NO and H₂ (or ¹⁵NO and H₂) were pulsed over pre-reduced, pre-oxidized or pre-nitrated catalysts with prescribed delay time (τ_d) and spacing time (τ_s).

Table 1. Physical properties of Pt/BaO/Al₂O₃ catalyst samples

	Sample D3	Sample B2M
Pt (wt%)	2.7	0.28
BaO (wt%)	14.6	16.6
Pt dispersion (%)	3	33
Mass of catalyst (mg)	110	97
Estimated number of exposed Pt sites	2.8 x 10 ¹⁷	2.8 x 10 ¹⁷

Results and Discussion

NO pulse storage experiments were carried out at 250 °C on pre-reduced catalyst to compare NO decomposition and storage differences in the two catalysts. The NO storage capacity of the lower dispersion catalyst (D3)) exceeded that of the higher dispersion catalyst (B2M). This suggests that in the physical mixture, the bulk BaO/Al₂O₃ does not provide significant NO_x storage. Moreover, catalyst D3 had a higher production of N₂ during the initial NO pulses than the higher dispersion catalyst (B2M). This suggests that Pt sites on the larger Pt crystallites are more active for NO decomposition.

Similar experiments with labeled ¹⁵NO pulsing on pre-nitrated Pt/BaO/Al₂O₃ catalysts (using unlabeled NO) provide evidence for a dynamic equilibrium between the gas and Pt as well as between Pt and BaO. Moreover, the sustained production of ¹⁵N₂ over hundreds of pulses and a noted absence of ¹⁵NN and N₂ products suggest that the ¹⁵N₂ formation pathway is by decomposition of ¹⁵NO on Pt sites freed up by the storage of ¹⁵NO on the BaO phase by spillover.

Isotopic pump-probe experiments provide additional evidence of N₂ formation on bulk Pt and also direct evidence of spillover processes during storage and reduction. Sequential pulses of ¹⁵NO and H₂ were fed to a pre-nitrated Pt/BaO/Al₂O₃ catalyst (using unlabeled NO); see Fig. 1. The data show the production of N₂, ¹⁵N₂, and ¹⁵NN during ¹⁵NO and H₂ pulses over 400 pump-probe cycles. Unlabeled N₂ is produced by reverse NO_x spillover from the Ba phase to Pt/BaO interface, where it decomposes to form N₂. The principal role of excess H₂ is to scavenge oxygen adatoms formed during NO and ¹⁵NO decomposition, freeing up Pt sites. The excess hydrogen also reacts with NO or N at the Pt/Ba interfacial region to form NH₃, causing a smaller production of N₂ during the H₂ pulse compared to ¹⁵NO pulse. As unlabeled NO_x is depleted from the Ba phase, the formation of N₂ also declines. The formation of ¹⁵N₂ is evident from the onset and is sustained throughout the experiment, indicating that decomposition occurs on bulk Pt sites farther away from the Pt/BaO interface. In addition to N₂ and ¹⁵N₂, the mixed product ¹⁵NN is formed during ¹⁵NO pulse, providing evidence for the reverse spillover of stored NO_x from the Ba phase to Pt sites where N and ¹⁵N recombine. The production of ¹⁵NN decreases at the expense of an increase in ¹⁵N₂ as unlabeled stored NO_x is depleted. Ongoing experimental results will be presented that elucidate the role of the Pt/BaO interface during NSR, such as NO_x spillover from Pt to Ba phase and reverse spillover from Ba phase to Pt

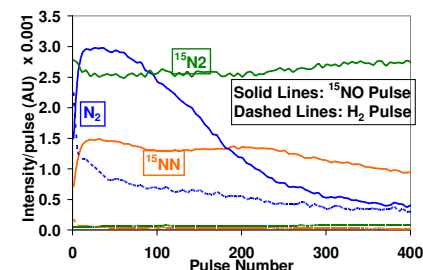


Figure 1. N₂, ¹⁵N₂ and ¹⁵NN profiles during ¹⁵NO/H₂ pump probe (H₂/¹⁵NO = 4.4) on pre-nitrated (with NO) on Pt/BaO/Al₂O₃ at 250 °C

Significance

There is a need for reducing NO_x emissions from the exhaust of lean burn gasoline and diesel engines. This work is a step towards gaining a fundamental understanding of the complex catalytic chemistry of NSR through systematic transient experiments and the development of microkinetic models.