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NO_x storage and reduction with H_2 on $Pt/BaO/Al_2O_3$ monolith: Spatio-temporal resolution of product distribution[☆]

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ABSTRACT

The regeneration of a model $Pt/BaO/Al_2O_3$ monolith catalyst was studied with hydrogen as the reductant to elucidate the reaction pathways to molecular nitrogen and ammonia. NO_x storage and reduction experiments (NSR) were conducted with a 2 cm length monolith for a wide range of feed conditions. The NSR experiments were replicated for a series of monoliths of progressively decreasing length, enabling the construction of spatio-temporal profiles of reactant and product concentrations. The results show that there are two primary competing routes to the desired N_2 product; specifically a direct route from the reduction of stored NO_x by H_2 ($H_2 + NO_x \rightarrow N_2$) or by a sequential route through NH_3 ($H_2 + NO_x \rightarrow NH_3$; $NH_3 + NO_x \rightarrow N_2$). A comparison between H_2 and NH_3 as reductant feeds during NSR revealed H_2 is a more effective reductant in terms of NO_x conversion for temperatures below approximately 230 °C. At higher temperatures (230–380 °C), the regeneration of stored NO_x is feed-limited and the difference between the reductants H_2 and NH_3 is found to be small with H_2 being a slightly superior reductant. Experimental measurements of the traveling front velocity are compared with a simple feed-limited model that assumes complete consumption of H_2 as stored NO_x is depleted. At lower temperatures the regeneration is limited by chemical processes at the Pt/Ba interface. The findings are pieced together to establish a phenomenological description of the spatio-temporal features of the lean NO_x trap with hydrogen as the reductant.

1. Introduction

Lean burn combustion encountered in lean burn gasoline and diesel vehicles provides for a higher fuel efficiency compared to stoichiometrically operated gasoline engines. However, the unconverted oxygen in the exhaust prevents the use of conventional three-way catalysts (TWC) in the reduction of NO_x to N_2. NO_x storage and reduction (NSR) is a periodic catalytic process for converting NO and NO_2 (NO_x) to N_2 that overcomes this obstacle. The inherent transient nature of NSR makes it highly complex, especially in terms of the spatio-temporal interactions of the storage and reduction catalytic processes. Advanced catalytic engineering is needed to elucidate the transient product distribution in particular since in most cases the objective is to convert NO_x to molecular nitrogen.

During NSR, the NO_x removal process involves two stages on a bifunctional supported catalyst. The first "storage" stage involves the reactive trapping of NO_x, in the form of nitrites or nitrates, on an alkali earth component (such as Ba, Ca, or Sr) enhanced by the catalytic oxidation of NO to NO_2 on the precious metal (Pt, Rh). The typical duration of this stage is 30–90 s. The second "purge" or "regeneration" stage involves purging or regenerating with a rich pulse containing reductant(s), carried out before an unacceptable amount of NO_x breaks through during the storage. The rich pulse duration is only a few seconds. It is created through intermittent rich operation of the engine, producing a mixture of H_2, CO, and low molecular weight hydrocarbons, or through direct injection of fuel into the exhaust system.

Earlier studies of NSR focused on the storage process, which established that the primary steps are the catalytic oxidation of NO to NO_2 followed by NO_2 storage by the disproportionation

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mechanism [1–5]. The mechanistic details at the Pt/Ba interface remain elusive. Recent research has shifted to the kinetics of the regeneration process. Particular attention has been placed on H_2 because it is not only present in the exhaust during rich engine operation, but also it is catalytically generated by both steam reforming of exhaust hydrocarbons and water gas shifting of CO. Hydrogen has been shown to be the most effective reductant due to its high reactivity with O, H, and N adspecies which are present during conventional NSR operation. Hydrogen is uniquely reactive at low temperatures (below 200 °C) [6–9]. The mechanism of NO_x reduction under cycling conditions is still not fully understood. Muncrief et al. [10] suggested a thermally driven process under conditions in which a relatively large concentration of O_2 is present during the rich pulse, which is more typical of diesel applications. Liu and Anderon [7] proposed a spillover mechanism of reductant from the precious metal (Pt) to storage phase comprising barium nitrate, $Ba(NO_3)_2$. Their proposed mechanism involves the reductant reacting directly with $Ba(NO_3)_2$ forming $Ba(NO_2)_2$, which then releases the stored NO_x as NO. Nova et al. [11,12] studied the reduction process under nearly isothermal conditions and observed that the thermal decomposition of stored NO_x was not necessary to reduce the stored NO_x with H_2 since regeneration can occur at temperatures well below the temperature at which stored NO_x decomposes. They proposed that the reduction of stored nitrates involves a Pt catalyzed surface reaction and argued that the pathway only occurs when both components (Pt and BaO) are well dispersed on the same support (as opposed to physical mixtures of separate populations of supported Pt and BaO particles). A follow up study by Cant et al. [13] observed results similar to those of Nova et al. [11] when comparing a sample with Pt and BaO dispersed on the same support with a physical mixture of BaO/Al_2O_3 and Pt/SiO_2; Pt/SiO_2 was used instead of Pt/Al_2O_3 in order to rule out NO_x storage on the same support as Pt. The reverse spillover of NO_x from BaO to Pt has also been speculated to occur [13–17]. Cant et al. [13] studied the isotopic exchange rate of ^{15}NO and stored $^{14}NO_x$ during storage on the two system described above at 360 °C. They concluded that the forward and reverse spillover of NO_x is important since the exchange rate was more than five times faster for the $Pt/BaO/Al_2O_3$ sample than for the physical mixture. James et al. [14] proposed the "reverse" spillover mechanism to explain the decomposition of nitrates stored far from Pt. Zhou et al. [17] have described the nitrate ions as being mobile in the barium phase with the reaction occurring at the Pt/Ba interface. However, neither H_2 spillover to BaO nor the reverse spillover of NO_x to Pt has been proven to be the main mechanism. Medhekar et al. [18] studied pre-reduced, pre-oxidized, and pre-nitrated Pt/BaO catalysts, and proposed that there existed two distinct reduction sites on Pt crystallites on the supported catalyst. The first type of sites are located further from the Pt/Ba interface where H_2 scavenging of surface oxygen provides a clean surface for NO decomposition to N_2 and N hydrogenation to NH_3. The second type of sites is located at the Pt/BaO interface. At these sites H_2 oxidation, nitrate decomposition, and NO decomposition and reduction occur, producing a complex mixture of N_2, N_2O, and NH_3 which depends on the temperature and effective NO_x/H ratio.

The situation is further complicated by integral effects brought about by chemistry occurring downstream in the monolith channel, Choi et al. [19] applied spatially-resolved mass spectrometry, coined "Spaci-MS", to obtain spatial profiles of reactant and product profiles through the use of capillary probes positioned in multiple monolith channels along the length of the monolith. In their study, Choi et al. [19] showed that H_2 produced from the water gas shift reaction had only a minor effect on the NO_x release and reduction.

The effects of H_2O and CO_2 on the reduction of stored NO_x by H_2 have been investigated [20–22]. Lindolm et al. [20] observed that CO_2 had a promoting effect on NH_3 formation at low temperatures. Lietti et al. [21] observed that the reduction of stored NO_x is slower when CO_2 and H_2O are fed during the regeneration.

More recent studies have been carried out that have focused on the role of ammonia during NSR. Ammonia is an undesired product during conventional NO_x trap operation, however, it is a desired product in coupled LNT/SCR systems [23–25]. Pihl et al. [26] and Cumaranatunge et al. [27] proposed that NH_3 formed upstream by the reaction of feed H_2 and stored NO_x may be consumed downstream by its own reduction of stored NO_x [26,27]. Once formed, the generated N_2 flows down the reactor and out with the effluent. NH_3 has the complicating feature that it will readsorb and react downstream with stored NO_x. Pihl et al. [26] described the monolith reaction system by three sections: mostly regenerated, reductant front, and un-regenerated. They proposed that the reductant H_2 front moves through the entrance section of the monolith where the main reduction chemistry occurs. Cumaranatunge et al. [27] described the NH_3 as a hydrogen carrier, from which H adatoms react with stored NO_x to produce N_2. They showed that the effectiveness of NH_3 and H_2 under reductant limited conditions (350 °C) were similar. However, data were not presented by either of the two groups that conclusively prove the proposed picture. Xu et al. [28] showed that the steady-state selectivity of the reaction between H_2 and NO to N_2O, N_2, and NH_3 is largely dictated by the feed composition (H_2/NO ratio) and temperature under steady-state conditions. Clayton et al. [29] have shown that the reduction of NO by a co-feed of H_2 and NH_3 identifies H_2 as the superior reductant. To this end, under the complex spatio-temporal conditions encountered during the hydrogen regeneration of the NO_x trap, isolating the production of ammonia from its consumption is key to understanding the NO_x trap performance.

The objective of this study is to establish a more complete picture supported by experimental measurement of lean NO_x trap behavior during NSR using H_2 as a reductant. This is accomplished through bench-scale LNT measurements in which the concentrations of all reactants and products are measured. We utilize a novel approach to generate axial profiles of species concentrations over a range of conditions. An analysis of the product distribution reveals the different routes to the desired N_2 product, whether directly from the reduction of stored NO_x by H_2 or indirectly through an NH_3 intermediate. The data also provide information about the velocity of the moving hydrogen and ammonia fronts. The findings are pieced together to establish a phenomenological description of the spatio-temporal features of the lean NO_x trap with H_2 as the reductant.

2. Experimental

2.1. Catalyst samples

The catalyst samples used for these experiments were monolith catalysts provided by BASF Catalysts LLC (Iselin, New Jersey). Larger cylindrical cores (D = 3.8 cm, L = 7.6 cm) were cut using a dry diamond saw to smaller, nearly cylindrical shapes ($D \sim 0.8$ cm, L = 0.33–2 cm). The samples contained BaO with varying amounts of Pt on a γ-alumina washcoat support adsorbed on a cordierite structure (~62 channels/cm^2). The mass of washcoat material (m_{wc}) on each monolith piece (of L = 2 cm) was approximately 110 mg. The compositions and properties of the catalysts are given in Table 1. The methods used to characterize the catalysts were described previously [28]. The monoliths were then wrapped in Fiberfrax® ceramic paper that had been heat treated and then placed in a quartz tube flow reactor.