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Modeling the effects of Pt loading on NOx storage on $Pt/BaO/Al_2O_3$ catalysts

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ABSTRACT

Platinum plays an important, multi-functional role during NOx storage and reduction (NSR). Understanding and predicting the effect of Pt loading is essential to optimize the lean NOx trap. In this study, a microkinetic model is developed for NOx storage on a series of $Pt/BaO/Al_2O_3$ catalysts with a range of Pt loadings (0–3.7 wt.%). A classification of the Ba sites into two storage site populations, proximal and non-proximal (bulk), is presented. A simple model for estimating the capacities of the two Ba site populations using the Pt loading is used to explain trends in the storage of NO/O_2 and NO_2/O_2. The model integrates existing literature models for NO_2 storage on BaO/Al_2O_3, Pt-catalyzed NO oxidation to NO_2, and spillover chemistry involving NO_2. Wherever possible, simplifications in the model are made based on sensitivity analyses. Literature estimates of kinetic parameters are adjusted if estimates of spillover rate constants are not sufficient to predict the storage data. The dual-site model comprises proximal storage sites that participate in the spillover chemistry and non-proximal sites that involve NO_2 that is generated by the Pt-catalyzed NO oxidation. The model shows reasonable agreement with the measured storage of NO and NO_2 in O_2 at 340 °C for a range of storage times and Pt loading. The model helps to elucidate the storage dynamics and the roles of Pt and should be useful for incorporation into a complete NOx storage and reduction model. Some further refinements to the model are discussed.

1. Introduction

Lean-burn and diesel engines offer better fuel efficiency and reduced hydrocarbon and carbon monoxide emissions compared to stoichiometric gasoline engines. While the presence of excess oxygen improves the in-cylinder combustion of hydrocarbons, it is unfavorable for NOx reduction in emission aftertreatment systems.

NOx storage and reduction (NSR), a concept first proposed in the 1990s [1], is emerging as a promising approach to control mobile NOx emissions. Unlike the commercialized selective catalytic reduction, which can be operated at steady-state but requires ammonia as a reductant, NSR is a periodically operated catalytic process that utilizes the fuel itself or fuel oxidation products (CO, H_2) as the reductant. The lean NOx trap (LNT), within which NSR is carried out, contains a multi-functional monolith catalyst comprising precious metals (Pt, Rh) and an alkaline-earth metal oxide (e.g. BaO) supported on a high surface area support (γ-Al_2O_3). During the lean phase of the cycle, exhaust NOx in the presence of excess oxygen is stored on the metal oxides in the form of nitrites and nitrates for up to a few minutes. Before significant NOx breakthrough occurs, either the engine is run rich or reductant is injected into the exhaust to produce a rich mixture for a much shorter duration, typically less than 10 s. This rich phase serves to reduce the stored NOx and regenerate the NSR catalyst for use in the next cycle. In order to achieve efficient NOx storage and reduction, rather high Pt loadings (1–2 wt.%) are needed in comparison to less than 0.2% typical of three way catalytic (TWC) converters [2].

Both bench-scale experiments and engine/vehicle tests show that NSR is a promising approach to reduce NOx emission from lean-burn engines. Efficient NOx trapping and time-averaged NOx conversions exceeding 90% have been obtained under cycle-averaged lean conditions [3–5]. In order to achieve theses conversions at high space velocities typical of emission aftertreatment devices, efficient NOx storage during the lean phase is crucial. During the early stage of NSR development, the research was mainly focused on NOx storage, especially, on $Pt/BaO/Al_2O_3$ catalysts. A large number of studies have been reported in the literature, which have been discussed in reviews [6–8].

The NOx exhaust from lean burn and diesel engines comprises mainly NO, which is thermodynamically favored over NO_2 at the high temperatures of the internal combustion. However, unlike NO_2, NO cannot be efficiently stored on BaO/Al_2O_3 catalysts without precious metal [2,9]. While the working principle of NSR is to trap NOx and then reduce it under intermittent rich conditions, a fraction of O_2 in the exhaust is utilized to oxidize NO to NO_2. Platinum has typically demonstrated the highest NO oxidation activity in catalysts containing BaO/Al_2O_3 [10–12], although Huang et al.

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[13] showed that Pd is effective in CaO/Al_2O_3 catalysts. Olsson and Fridell [14] and Muncrief et al. [4] observed that the addition of BaO to Pt/Al_2O_3 catalysts reduces the NO oxidation activity. Xue et al. [15] investigated the effects of support material, Pt loading and Pt dispersion during NO oxidation. They reported that SiO_2 is a superior support for Pt catalyzed NO oxidation, followed by Al_2O_3 and ZrO_2. They also reported that an optimal Pt particle size exists on both SiO_2 and Al_2O_3.

The effects of feed constituents of O_2, NO and NO_2 on the rate of NO oxidation have been studied extensively [16–21]. It is generally agreed that the NO oxidation rate is positive order in O_2 and NO but is negative order in NO_2. Olsson et al. [18] developed a microkinetic model to predict their experimental findings. Muncrief et al. [3] and Marques et al. [22] reported a positive order dependence of NO oxidation rate on NO and O_2. Mulla et al. [19,23] studied NO oxidation kinetics and found the rate order in NO_2 is approximately −1. Bhatia et al. [24] showed that O_2 adsorption and desorption are the rate limiting steps for NO oxidation and NO_2 decomposition, respectively. These results are consistent with a more recent study by Weiss and Iglesia [25].

Several reaction pathways have been proposed to describe NOx storage on $Pt/BaO/Al_2O_3$ catalysts. For storage time longer than a few minutes, the storage of NO_2, either directly fed or produced by catalytic NO oxidation, follows the disproportionation mechanism with $Ba(NO_3)_2$ as the final product [2]:

$$3NO_2(g) + BaO(s) \leftrightarrow Ba(NO_3)_2(s) + NO(g)$$

Pt provides another pathway for NOx storage. Takahashi et al. [1] compared the $Pt/BaO/SiO_2$ catalyst to a physical mixture of Pt/SiO_2 and BaO/SiO_2 and found that the physical mixture has a much lower NOx storage than $Pt/BaO/SiO_2$. This is a clear indication of spillover reactions between the two catalyst components. Epling et al. [26] proposed that the longer term disproportionation occurs on barium sites far from Pt clusters while the initial storage of NOx occurs on barium sites in the close proximity to Pt clusters. O adatoms on Pt were proposed to oxidize the storage component from nitrites to nitrates. The spillover of O–Pt was also proposed by Fridell et al. [27]. Kabin et al. [2] suggested a "hybrid" pathway consisting of three steps. Instead of O adatoms, NO_2 admolecules on Pt were proposed by Paterson et al. [28] to react with storage species on barium.

NOx storage on $Pt/BaO/Al_2O_3$ catalysts has been optimized in the temperature range of 300–380 °C for a feed containing NO and O_2 [5,29]. It was also reported that the storage of an NO_2 feed is more efficient than an NO/O_2 feed [30,31]. Fridell et al. [25] reported that the difference is negligible at higher temperatures. They also found that the increase in O_2 concentration up to 3% enhances the NOx storage. This may be due to the positive effects of O_2 on catalytic NO oxidation, as stated previously. Another reason is that an increased O_2 concentration shifts the thermodynamic equilibrium of the NOx storage reactions [32].

Most NOx storage studies have been carried out on supported BaO, with or without precious metals. NOx can also be adsorbed on the alumina support [28,29]. In order to avoid the complicating effects of precious metals and support materials, Yi et al. [33] conducted NO_2 storage experiments on a thick BaO layer supported on an Al_2O_3/NiAl substrate. They showed that the decomposition of a nitrite leaves O, forming BaO_2, which is more thermally stable than nitrates. It was also found that the surface nitrate formation occurs on alumina supported BaO but not on unsupported BaO. This feature indicates interactions between the high surface area alumina support and BaO.

Platinum plays an important role during NOx storage due to NO oxidation and spillover reactions. Given its cost, there is a need to reduce the Pt loading in the LNT. To this end, understanding the effect of Pt loading and dispersion effects on NOx storage is essential. A kinetic model of NOx storage is needed that predicts Pt loading effects in order to help in the optimization of NSR catalysts that not only have high storage efficiency but also have a minimal amount of Pt. To the best of our knowledge, such a model has not appeared in the literature. Thus, the objective of this study is to develop a mechanistically based kinetic model that predicts Pt loading effects on NOx storage.

The paper is organized as follows. First a brief review of the detailed experimental study of Pt loading effects on NOx storage by Kabin et al. [2] is given. Then the main elements of the storage model are described consistent with these data and adapted from previous literature models. The approach taken first considers NO and NO_2 storage on BaO (Pt free) catalyst, and then couples with that a previously developed NO oxidation kinetic model as well as a treatment of spillover chemistry. Sensitivity analyses are conducted to simplify the chemistry based on the data trends. Finally, the model predictions are discussed in the content of a phenomenological picture of NOx storage on $Pt/BaO/Al_2O_3$ catalysts.

2. Review of NOx storage experiments

Kabin et al. [2] carried out storage measurements of NO and NO_2 (in O_2) on a series of $Pt/BaO/Al_2O_3$ catalysts with Pt loadings varied between 0 and 3.7 wt.% (based on washcoat). The effluent NO and NO_2 concentrations were measured to investigate the promoting effects of Pt on NOx storage. The experimental operating parameters and catalyst properties are listed in Table 1 while representative data are shown in Figs. 1 and 2. The main experimental trends are summarized as follows:

- NO storage on BaO/Al_2O_3 in the presence of O_2 without Pt is negligible but measurable.
- In contrast, NO_2 storage in the presence of O_2 on BaO/Al_2O_3 is significant.
- Pt enhances the storage of both NO and NO_2 in the presence of O_2. A small amount of Pt significantly increases the storage of NOx. The trend confirms that the Pt catalyzes NO oxidation, producing NO_2 which readily stores on BaO.
- Platinum also enhances the storage of NO_2. This trend suggests that spillover chemistry occurs at the interface of Pt crystallites and BaO storage sites, which increases the storage of NO_2.
- The Pt enhancement effect diminishes at higher loadings for both NO and NO_2 storage in the presence of O_2.
- At longer exposure time and lower Pt loadings, the disproportionation ratio ($3NO_2$ consumed/1 NO released) is satisfied during NO_2 storage.
- The effluent concentration of total NOx ($NO + NO_2$) generally decreases monotonically with increased Pt loading for a fixed storage time, for both NO/O_2 and NO_2/O_2 feeds.
- The NO (NO_2) is a nonmonotonic function of the Pt loading for a fixed storage time for the NO_2/O_2 (NO/O_2) feed.

Additional NO_2 storage experiments were carried out more recently in our laboratory to compare NO_2 uptake in the absence of gas phase O_2 on the BaO/Al_2O_3 catalyst (B0) at a slightly higher

Table 1
Reactor parameters for NOx storage experiments (Kabin et al. [2]).

Monolith reactor		Catalyst sample	BaO loading (wt.%)	Pt loading (wt.%)	Pt particle size (nm)
Length	2 cm				
Diameter	0.8 cm	B0	16.7	0.00	–
$N_{channel}$	62 per cm^2	B1	16.6	0.32	2.85
Flowrate	1 SLPM	B2	16.5	1.27	3.43
$m_{washcoat}$	≈0.1 g	B3	16.3	2.20	5.18
Temp.	340 °C	B4	16	3.71	3.26

Feed composition: 500 ppm NO or NO_2; 5% O_2; N_2 carrier.