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# Model for $NO_x$ storage/reduction in the presence of $CO_2$ on a Pt–Ba/$\gamma$-$Al_2O_3$ catalyst

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## Abstract

We have constructed a global reaction kinetic model to better understand and describe the $NO_x$ storage/reduction process in the presence of $CO_2$. Experiments were performed in a packed-bed reactor with a Pt–Ba/$\gamma$-$Al_2O_3$ powder catalyst (1 wt% Pt and 30 wt% Ba) with different lean/rich cycle timings. The model is based on a multiple storage sites mechanism and considers that fast $NO_x$ storage occurs at surface barium sites, as determined by the reaction kinetics. Slow $NO_x$ storage occurs at the semi-bulk and bulk barium sites, where diffusion plays a major role. It is assumed that surface, bulk, and semi-bulk sites differ not only in physical appearance, but also in chemical reactivity. The distribution of these sites is obtained from 9-h lean-phase and 15-h rich-phase cycling experiments and thermogravimetric analysis of fresh catalyst. The model adequately describes the NO and $NO_2$ breakthrough profiles during 9 h of lean exposure, as well as the subsequent release and reduction of the stored $NO_x$. Furthermore, the model is also capable of simulating transient reactor experiments with 240-s lean-cycle and 60-s rich-cycle timings.

*Keywords:* $NO_x$ trap; Barium nitrate; Lean-burn; Model; $NO_x$ storage; $NO_x$ reduction; Emissions; $NO_x$ storage and reduction

## 1. Introduction

The popularity of diesel and lean-burn engines is increasing due to their better fuel efficiency and lower emission of the greenhouse gas $CO_2$ compared with conventional gasoline engines. However, achieving oxidation of CO and hydrocarbons simultaneously with $NO_x$ reduction in the exhaust is challenging for lean-burn engines, in which excess $O_2$ in the exhaust gas hinders the reduction of $NO_x$. One promising approach to reducing $NO_x$ during lean exhaust operation is the use of $NO_x$ storage reduction (NSR) catalysts [1]. The most widely investigated NSR catalytic systems are Pt-based oxidation catalysts, which contain barium as a storage component. Under fuel-lean conditions, with excess $O_2$, $NO_x$ is stored on the barium as nitrites/nitrates. As the storage capacity of barium is saturated, the catalyst must be regenerated. For regeneration, extra fuel is injected, resulting in a fuel-rich period during which $NO_x$ is released and reduced to $N_2$. Understanding the NSR mechanism is crucial for reducing catalyst regeneration times and preventing catalyst deactivation. Unfortunately, the NSR catalysts have shown serious deactivation in the presence of $SO_2$ [2].

The NSR process has been the focus of several kinetic studies (see [3] and references herein); however, there is no clear agreement on the steps by which $NO_x$ storage occurs. It is generally believed that NO is first oxidized to $NO_2$ over Pt sites. $NO_2$ is stored in the form of barium nitrate [4–7]. $NO_2$ storage can also proceed via a disproportionation route, resulting in nitrate formation and NO release in the gas phase [4,5,8]. There is growing evidence that in the presence of $O_2$, NO can be stored directly as barium nitrite [4,9]. In addition, the contribution of direct NO storage increases with increasing barium loading [10]. Nitrites can be further oxidized into nitrates with $NO_2$ as an oxidizing agent [11–13]. Furthermore, several studies have aimed to gain insight into the effect of different reductants in the fuel-rich phase. James et al. found that CO facilitates $Ba(NO_3)_2$ decomposition, but not $NO_x$ reduction [14]. However, $H_2$ enables both to occur with high conversion to $N_2$.

In general, three different time periods can be distinguished during fuel-lean exposure. In the first period, complete $NO_x$

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storage occurs. During the second period, $NO_x$ breakthrough with considerable $NO_x$ storage is observed. The third period is characterized by slow $NO_x$ storage and persists longer than the other two periods. The three different time periods indicate the presence of multiple types of barium sites with different reactivities toward $NO_x$ storage [15]. Barium sites located close to Pt sites are considered more reactive than barium sites located farther away [16]. Barium can be present in the catalyst as BaO, $Ba(OH)_2$, and $BaCO_3$, depending on the reaction conditions [7]. $NO_x$ storage occurs preferentially at BaO, then at $Ba(OH)_2$, followed by $BaCO_3$ sites. Recently, low-temperature (LT) and high-temperature (HT) barium-containing species have been distinguished [17,18]. The crystalline bulk-like HT-barium sites are thermally more stable than the well-dispersed LT-barium phase. The LT-barium sites show a higher activity toward $NO_x$ storage and reduction than the HT sites [19,20]. With an increase in total barium loading, the number of LT sites initially increases, reaching a constant maximum value at a barium loading of about 17% (w/w) [18,19]. The HT phase also increases with barium loading, without saturation.

Although there is clear evidence in the literature that multiple types of barium sites exist, models of the NSR process are based mostly on a single type of reaction site. Olsson et al. [21] developed an elementary kinetic model, but this model could not describe the decreasing $NO_x$ trapping activity observed as the lean phase proceeded. Global models based on shrinking core mechanisms have been used to describe the $NO_x$ storage process [22–25]. In general, these models assume that $NO_x$ diffusion inside the barium clusters or $NO_x$ transfer to the barium sites is the rate-controlling step in the $NO_x$ storage process. The presence of an inactive barium core has been assumed to describe the observed incomplete barium utilization [23]. In all of these models, no distinction is made between reactivity of surface and bulk barium sites toward $NO_x$ storage.

Furthermore, the vehicle exhaust gas always contains $CO_2$ and $H_2O$. However, most studies do not take into account the presence of these species. It has been reported that $CO_2$ negatively affects the $NO_x$ storage process [15,26,27], whereas $NO_x$ release studies have shown that $CO_2$ has a promoting effect on $NO_x$ release in the fuel-rich phase [26,28,29]. The $H_2O$ effect is limited to the $NO_x$ storage process mainly at low temperatures (below 300 °C) [26].

The goal of the present work is to develop a global reaction kinetic model based on a multiple–storage sites mechanism for the NSR process in the presence of $CO_2$. In addition, the model provides a better understanding of reaction steps and barium utilization during the NSR process at different time scales. Experiments have been performed in a packed-bed reactor with a Pt–Ba/$\gamma$-$Al_2O_3$ powder catalyst (1 wt% Pt and 30 wt% Ba) with different lean-cycle/rich-cycle timings. The contributions of the different barium sites and the model parameters have been deduced from 9-h lean-cycling/15-h rich-cycling experiments. The model was validated for other conditions, including different NO concentrations and different $H_2$ concentrations. In addition, cycle times of 240 s lean and 60 s rich have been used to demonstrate the applicability of the developed model for lean/rich timings under conditions more closely resembling automotive exhaust conditions. NO is used as the $NO_x$ source, whereas $H_2$ is used as the reducing agent. Catalyst characterization using thermogravimetric analysis (TGA) combined with mass spectrometry (MS), XRD, BET analysis, and Pt dispersion measurement has been done to support the model results.

## 2. Experimental

### 2.1. Alternation of lean and rich flows

Lean/rich cycling experiments were performed in a packed-bed reactor, as described previously [30]. The gas composition of reactants and products was measured with an on-line quadrupole mass spectrometer (ESS). A fixed amount of argon was fed as an internal standard during experiments to compensate for any intensity loss of the mass spectrometer. Gas analysis was performed on $m/e$ 2 ($H_2$), 17 ($NH_3 + H_2O$), 18 ($H_2O$), 28 ($N_2 + CO_2 + CO$), 30 ($NO + NO_2$), 32 ($O_2$), 40 (Ar), 44 ($CO_2 + N_2O$), and 46 ($NO_2$). A high-resolution magnetic sector mass spectrometer (Jeol JMS GCmate) was also used for the analysis of $N_2 + CO$ and $CO_2 + N_2O$. It was verified that external and internal diffusion limitations were absent at the scale of the catalyst pellet. A $NO_x$ storage catalyst, Pt–Ba/$Al_2O_3$ (1/30/100 w/w/w), was used in powder form as provided by Engelhard. Typically, 1.9 g of catalyst with an average pellet diameter of 180 µm was used in the $NO_x$ storage/reduction experiments. The fresh catalyst was pretreated at 773 K with 1 vol% of oxygen in helium for 1 h, followed by 0.5 h in helium, and finally by reduction with 2 vol% of hydrogen in helium for 2 h. The total gas flow during the experiments was kept constant at 0.743 mmol/s, resulting in a gas hourly space velocity (GHSV) of 29,000 $h^{-1}$ (standard conditions, 298 K and 1 bar). Table 1 shows the experimental conditions for the lean/rich cycling experiments.

Table 1
Experimental conditions of lean/rich cycling experiments

| | Temperature (K) | Inlet lean[a] | Inlet rich[a] |
|---|---|---|---|
| 9 h lean/15 h rich | 513, 573, 643 | 0.2 vol% NO<br>4 vol% $O_2$<br>10 vol% $CO_2$<br>1 vol% Ar | 0.8 vol% $H_2$<br><br>10 vol% $CO_2$<br>1 vol% Ar |
| | 573 | 0.3 vol% NO<br>4 vol% $O_2$<br>10 vol% $CO_2$<br>1 vol% Ar | 0.8 vol% $H_2$<br><br>10 vol% $CO_2$<br>1 vol% Ar |
| | 573 | 0.2 vol% NO<br>4 vol% $O_2$<br>10 vol% $CO_2$<br>1 vol% Ar | 1.2 vol% $H_2$<br><br>10 vol% $CO_2$<br>1 vol% Ar |
| 4 min lean/1 min rich | 573 | 0.2 vol% NO<br>4 vol% $O_2$<br>10 vol% $CO_2$<br>1 vol% Ar | 0.8 vol% $H_2$<br><br>10 vol% $CO_2$<br>1 vol% Ar |

[a] He is carrier gas.