



# Kinetic modeling of sulfur poisoning and regeneration of lean NO<sub>x</sub> traps

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## ABSTRACT

Sulfur poisoning and regeneration of lean NO<sub>x</sub> traps were investigated using experiments and kinetic modeling. A commercial Pt, Rh and barium containing NO<sub>x</sub> storage catalyst was used. The catalyst also contained oxygen storage material. First the oxygen storage capacity (OSC) was investigated using steps with oxygen and hydrogen. The OSC was substantial with a total use of all hydrogen (1%) for about 20 s. The results were similar at the three investigated temperatures (300, 400 and 500 °C), indicating that it is a low activation barrier connected with the process. Further, no effect was observed when adding 15 ppm SO<sub>2</sub> to the feed. Since no SO<sub>2</sub> was observed in the outlet it is possible that SO<sub>2</sub> is adsorbed during the lean period and then reduced to form H<sub>2</sub>S in the rich period (not measured). Further, the NO<sub>x</sub> storage was found to decrease during SO<sub>2</sub> exposure, and the decrease was linear and dose dependent. In addition, we investigated different regeneration strategies. When using 500 ppm H<sub>2</sub> for 60 min at 700 °C the regeneration was poor. However, when adding 5% CO<sub>2</sub> to the 500 ppm H<sub>2</sub> the regeneration was increased drastically. Further, the regeneration was decreased when decreasing the temperature to 600 °C, and further decreased when using 500 °C. In addition, it was beneficial with increasing the hydrogen concentration. The kinetic model contains three sub-models: (i) NO<sub>x</sub> storage and regeneration, (ii) oxygen storage and reduction and (iii) sulfur poisoning and sulfur regeneration. It was crucial to add NO<sub>x</sub> storage on two sites; barium and alumina. The NO<sub>x</sub> adsorbed on alumina is more loosely bound. Further, in the model formation of sulfates were added on both components. This was important in order to describe the rate of the sulfur deactivation. If sulfur was adsorbed only on barium the deactivation would have been too rapid. The model could describe the experimental features well.

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## 1. Introduction

Diesel and lean burn gasoline engines have a lower fuel consumption compared to conventional stoichiometric gasoline engines. However, due to the large oxygen excess in these exhausts it is important to decrease the nitrogen oxides (NO<sub>x</sub>) emissions due to environmental reasons, since the standard three-way catalyst (TWC) will be oxygen poisoned. One concept is lean NO<sub>x</sub> traps (LNT), also called NO<sub>x</sub> storage and reduction (NSR) and lean NO<sub>x</sub> adsorbers (LNA). The engine is altered between lean (oxygen excess) and rich (fuel excess) operation. During the lean period the catalyst stores the NO<sub>x</sub> and during the rich periods the NO<sub>x</sub> is release and reduced on the noble metal sites. Several studies have shown that sulfur poisons the NO<sub>x</sub> storage capacity using several experimental techniques like flow reactor experiments [1,2], in situ FTIR [3–6], X-ray photo emission spectroscopy (XPS) [1,7], X-ray absorption spectroscopy (EXAFS) [5], temperature programmed desorption (TPD) [8], X-ray diffraction (XRD) [9] and energy dispersive X-ray spec-

troscopic (EDX) [9]. It is observed that the deactivation of the NO<sub>x</sub> storage capacity is proportional to the total SO<sub>2</sub> dose and is not affected by the SO<sub>2</sub> concentration [1]. Further, deactivation was larger when SO<sub>2</sub> was present in the rich condition compared to in the lean period [10]. Corbos et al. [11] observed close to complete regeneration in rich conditions at 550 °C. Further, Poulston and Rajaram [7] found that the sulfur regeneration was increased when CO<sub>2</sub> was present.

There are some kinetic models present in the literature for lean NO<sub>x</sub> traps. Olsson et al. [12,13] and Tuttlies et al. [14] use a shrinking core type of model for describing mass-transport resistance within the barium particles. Scholz et al. [15] presented a global reaction kinetic model based on a multiple storage site mechanism using hydrogen as reducing agent. However, the ammonia production was not included in this model. Laurent et al. [16] presented a global model for NO<sub>x</sub> storage and Koci et al. [17] presented a kinetic model for NO<sub>x</sub> storage and regeneration using hydrogen including ammonia formation. Bhatia et al. [18] presents a two sites global kinetic model for NO<sub>x</sub> storage and reduction, using H<sub>2</sub> as reducing agent. In a recent publication Koci et al. [19] presents a model that can describe the effect of using different reducing agents. A series of papers by Olsson and co-workers describe a detailed kinetic

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## Nomenclature

### Parameter

$a_j$	active site density for reaction $j$ (mol-sites/m <sup>3</sup> )
$A$	pre-exponential factor (Unit depends on rate expression. The concentrations in the rates are in mol/m <sup>3</sup> and the rates in unit s <sup>-1</sup> .)
$A_{\text{tot}}$	front area of the monolith (m <sup>2</sup> )
$C_{g,\text{tot}}$	the total concentration in the gas bulk, where the temperature is $T_g$ (mol/m <sup>3</sup> )
$c_{s,i}$	the molar concentration of the gas specie $i$ at the catalyst surface (mol/m <sup>3</sup> )
$C_{s,\text{tot}}$	the total concentration at the catalyst surface, where the temperature is $T_s$ (mol/m <sup>3</sup> )
$D_h$	hydraulic diameter of channel (m)
$D_{i,m}$	binary diffusion coefficient of specie $i$ in the mixture (m <sup>2</sup> /s)
$E_a$	activation energy (J/mol)
$k$	rate constant (Unit depends on rate expression. The concentrations in the rates are in mol/m <sup>3</sup> and the rates in unit s <sup>-1</sup> .)
$k_{m,i}$	mass-transfer coefficient for specie $i$ (mol/(m <sup>2</sup> s))
$n_{\text{cycle},3}$	NO <sub>x</sub> storage capacity in cycle 3 (μmol)
$N_r$	number of reactions
$n_{\text{SO}_2}$	amount of SO <sub>2</sub> exposure per cycle (μmol)
$n_{\text{theoretical}}$	theoretical NO <sub>x</sub> storage capacity (μmol)
$n_{\text{ocycles}}$	number of cycles with SO <sub>2</sub> present
$Sh$	Sherwood number
$P_{\text{tot}}$	total pressure (Pa)
$r_j$	reaction rate for reaction $j$ (mol/(mol-sites s))
$R$	gas constant (J/(mol K))
$S_{ij}$	stoichiometric coefficient of specie $i$ in reaction $j$
$S_{kj}$	stoichiometric coefficient of surface specie $k$ in reaction $j$
$S$	surface area per reactor volume (m <sup>-1</sup> )
$t$	time (s)
$T_s$	temperature at catalyst surface (K)
$w$	molar flow rate (mol/s)
$x_{g,i}$	mole fraction of gas specie $i$
$x_{s,i}$	mole fraction of gas specie $i$ at the surface
$z$	axial position (m)
$\alpha$	constant
$\theta_k$	coverage of component $k$

model for NO<sub>x</sub> storage with thermal regeneration [20], propene regeneration [21], hydrogen regeneration including ammonia formation [22] and sulfur poisoning [23]. The kinetic model for sulfur poisoning is developed using sulfur exposure before temperature programmed desorption experiments with NO<sub>2</sub> [23]. However, there are today no kinetic models available that can describe the sulfur poisoning during lean rich cycling and the regeneration of the formed sulfates, which is the objective with this work.

## 2. Experimental

A commercial NO<sub>x</sub> storage catalyst was used in this work. The catalyst contains Pt, Rh, barium and oxygen storage components. The catalyst was aged in a reactor by:

- 750 °C: 5 min stoichiometric and 1 min lean exposures for 1 h. Stoichiometric conditions: 9000 ppm CO, 500 ppm NO, 1100 ppm C<sub>3</sub>H<sub>6</sub> and 9200 ppm O<sub>2</sub>. Lean conditions: 9000 ppm CO, 500 ppm NO, 1100 ppm C<sub>3</sub>H<sub>6</sub> and 8% O<sub>2</sub>.
- 850 °C: 1 h in Ar

- Saturation of the sample with sulfur during mixed lean and rich conditions at 400 °C for 25 cycles.

Lean periods (11 min): 500 ppm NO, 0.5% CO<sub>2</sub>, 8% O<sub>2</sub> and 15 ppm SO<sub>2</sub>.

Rich periods (4 min): 500 ppm NO, 0.5% CO<sub>2</sub>, 10,000 ppm H<sub>2</sub> and 15 ppm SO<sub>2</sub>.

Long lean rich cycles were used in order to have a large breakthrough of NO<sub>x</sub>. This is done to facilitate the modeling development. The catalyst was a monolith, which was 30 mm long and 21 mm in diameter. The catalyst was placed in a quartz tube with one thermocouple placed inside the catalyst and one about 1 cm in front of the sample. The gases were mixed using several mass flow controllers and the gases in the outlet feed stream was analyzed using a gas FTIR (MultiGas™ 2030). The total flow was 3500 ml/min which corresponds to a space velocity of 20,000 h<sup>-1</sup>.

For the OSC measurements the catalyst was exposed to lean rich cycling. The gas composition was for lean conditions (11 min): 8% O<sub>2</sub>, 0.5% CO<sub>2</sub>, 15 ppm SO<sub>2</sub> and for rich conditions (4 min): 10,000 ppm H<sub>2</sub>, 0.5% CO<sub>2</sub>, 15 ppm SO<sub>2</sub>. The first three cycles were sulfur free. The experiment was conducted at 300, 400 and 500 °C.

For the NO<sub>x</sub> storage measurements cyclic experiments were conducted. 13 cycles were done in each experiment, with the first three free of sulfur. The gas composition was: Lean periods (11 min): 500 ppm NO, 0.5% CO<sub>2</sub>, 8% O<sub>2</sub> and 15 ppm SO<sub>2</sub> and rich periods (4 min): 500 ppm NO, 0.5% CO<sub>2</sub>, 10,000 ppm H<sub>2</sub> and 15 ppm SO<sub>2</sub>. The catalyst was regenerated between each experiment with 500 ppm H<sub>2</sub> + 5% CO<sub>2</sub> for 60 min at 700 °C. The cycling at 400 °C, with the subsequent regeneration, was repeated in order to investigate the reproducibility. Further, cycling was also conducted at 300 and 500 °C, with regeneration at 700 °C using 500 ppm H<sub>2</sub> + 5% CO<sub>2</sub> for 60 min. Further, the effect of varying the regeneration was investigated. These experiments were followed by lean rich cycling experiments at 400 °C (same sequence as described above). The following regenerations were investigated: (i) 500 ppm H<sub>2</sub> + 5% CO<sub>2</sub> for 60 min at 700 °C, (ii) 500 ppm H<sub>2</sub> + 5% CO<sub>2</sub> for 60 min at 600 °C, (iii) 500 ppm H<sub>2</sub> + 5% CO<sub>2</sub> for 60 min at 500 °C, (iv) 500 ppm H<sub>2</sub> for 60 min at 700 °C, (v) 5000 ppm H<sub>2</sub> + 5% CO<sub>2</sub> for 60 min at 700 °C.

## 3. Catalyst model

The material balances were solved using FORTRAN.

The main governing equation for the gas phase species is:

$$\frac{w}{A_{\text{tot}}} \frac{\partial x_{g,i}}{\partial z} = -k_{m,i} S (x_{g,i} - x_{s,i}) = \sum_{j=1}^{nr} a_j S_{ij} r_j(T_s, c_s, \theta) \quad (1)$$

The coverage of component  $k$  on the surface is solved by:

$$\frac{d\theta_k}{dt} = \sum_{j=1}^{nr} S_{kj} r_j(T_s, c_s, \theta) \quad (2)$$

The relationship between the concentration and the molar fraction is:

$$C_{s,i} = C_{s,\text{tot}} x_{s,i} \quad (3)$$

where

$$C_{s,\text{tot}} = \frac{P_{\text{tot}}}{RT_s} \quad (4)$$

The film model is used to describe the mass-transfer between the gas and the catalyst surface, which is the middle term in Eq. (1) above. The mass-transfer coefficient was calculated using the Sherwood number ( $Sh = 3$ ):

$$k_{m,i} = \frac{Sh}{D_h} (C_{g,\text{tot}} D_{i,m}) \quad (5)$$

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