

# Investigations of chemical processes in a NOx-storage catalyst by the use of detailed chemistry and flow analysis

K. Fröjd<sup>1</sup>, F. Mauss<sup>2</sup>

<sup>1</sup> Lund Combustion Engineering - LOGE AB,  
Ideon Science Park, Scheelev. 17, 223 70 Lund, Sweden,  
e-mail: kfrojd@loge.se

<sup>2</sup> Dept. of Thermodynamics and thermal process engineering, Brandenburg University of Technology,  
Sielower Straße 12, DE-03044 Cottbus, Germany

## Abstract

Element flow analysis is used to study a NOx-storage catalyst. A newly developed 1D transient catalyst model is used, employing detailed surface kinetics. Flow analysis is used to explain C<sub>3</sub>H<sub>6</sub> and CO inhibition of NO oxidation as well as H<sub>2</sub> acting as reducing agent for NO reduction. Important conclusions about the catalytic system are made. Flow analysis is shown to be a very useful tool to study heterogeneous reactions in catalysts.

## Introduction

Catalysts are crucial for emission reduction in modern combustion engine after-treatment systems. To predict the catalyst response during transient load cycles the chemical processes need to be understood in detail. For this purpose, simple and numerical fast but still accurate models are desired. In this paper a transient one-dimensional catalyst model is used [1]. This model makes use of two zones, treating the bulk gas and washcoat separately. Heat and mass transfer between the zones are simulated by the use of heat and mass transfer coefficients, calculated from Nusselt and Sherwood numbers. Surface chemistry is modelled by detailed or global surface chemistry in the thin film layer, and gas phase chemistry can be treated in both zones.

The model usability has been demonstrated in a separate publication [1]. In this work the reaction paths inside a Pt- $\gamma$ -alumina washcoat catalyst are studied. Detailed surface chemistry [3] is applied, and flow analysis is used to study the heterogeneous reaction steps. Important conclusions are drawn about the system, and conclusions drawn in [1] are scrutinized. It is shown that flow analysis can provide further insight to the chemical processes in catalysts, thus enhancing the understanding of after-treatment systems.

## Specific Objectives

The main objective of this paper is to deepen the knowledge about NO conversion and reaction paths in Pt- $\gamma$ -alumina washcoat catalysts. Element flow analysis is demonstrated to be an excellent tool to understand such systems.

## Model Description

The catalyst is modeled by a number of representative channels in which gas and surface properties are calculated as functions of axial distance. In this work the single-channel approach is used.

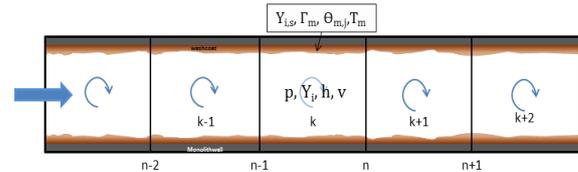


Figure 1 - Illustration of channel model

The channel is discretized into a finite number of sections of length  $\Delta x$  (see Figure 1). In each channel section the bulk gas is modeled as a perfectly stirred reactor (PSR). To account for external diffusion the gas close to and inside the washcoat is modeled as a separate zone, called the *thin film layer*. Heat and mass transfer coefficients are calculated from boundary layer theory, using Nusselt and Sherwood number correlations for the actual geometry. The conservation equations for gas species mass fractions, gas enthalpy, surface temperature, thin film layer gas species mass fractions and surface site fractions are solved in each zone for each time step. The Navier-Stokes equations for pressure and flow velocity are solved over all sections in a separate step. In the thin film layer either detailed surface chemistry or global gas phase chemistry is used. When using detailed surface chemistry, three global parameters are used to tune the model to a certain catalyst topology and composition; One parameter for heat transfer, one for mass transfer and one for overall reaction efficiency.

The model is integrated into the DARS [4] software for chemical reaction calculations.

The model is thoroughly described in [1].

## Flow Analysis

Flow analysis determines the mass flow of a given element from the reactants to the final products. The flow of element  $a$  from species  $j$  to species  $i$  at a given time,  $t$ , is defined by

$$F_{i,j}^a(t) = \sum_{R=1}^{N_R} r_R(t) \left( \nu_{jR}' \nu_{iR}'' - \nu_{jR}'' \nu_{iR}' \right) \frac{n_j^a n_i^a}{\Delta n_R^a}$$

where  $t$  is time,  $r_R(t)$  is the rate of reaction  $R$  at time  $t$ ,  $n_i^a$  is the number of atoms of type  $a$  in species

$i$ ,  $\nu_{jR}'$  is the left hand side stoichiometric coefficient of species  $j$  in reaction  $R$ ,  $\nu_{iR}''$  is the right hand side stoichiometric coefficient of species  $i$  in reaction  $R$  and  $\Delta n_R^a$  is the total flow of atom  $a$  in the reaction  $R$ :

$$\Delta n_R^a = \sum_{k=1}^{N_s} n_k^a (\nu_{kR}'' - \nu_{kR}')$$

where  $N_s$  is the number of species in the mechanism. The element flow for all species is combined to a flow chart, where the arrow thickness represents the values of  $F_{i,j}^a(t)$ . See e.g. Fig. 3.

### Experimental Data and Model Parameters

The model is applied to experiments (published elsewhere [2], [3]) simulating fuel rich and fuel lean exhaust engine emissions in a flat-bed reactor. The catalyst is equipped with lateral outlets, giving the possibility to measure and study gas concentration profiles along the length of the catalyst. The experimental setup, measurements and catalyst used is thoroughly described in Ref. [2] and [3]. Next follows a brief description of the setup.

The experiments are carried out under isothermal and steady state conditions in a flat-bed reactor manufactured by Delphi catalyst. The catalyst used is a platinum  $\gamma$ -alumina washcoat carried by a monolithic honeycomb structure (10319) ([2], [3]). See Table 1 for reactor specifications.

**Table 1 – Specifications of the flat bed reactor**

Slice length	40 mm
Slice width	30 mm
Slice height	One channel width
Total length	0.2 m
Channel diameter	1.0 mm
Channel density	400cps
Wall thickness	0.1524 mm
Washcoat	Pt/Al <sub>2</sub> O <sub>3</sub>
Platinum dispersion	16 %
BET surface area	49 m <sup>2</sup> /g
Median pore diameter	10 nm
Washcoat porosity	40 %

The space velocity of the gas is 40000 h<sup>-1</sup>. A realistic model exhaust gas for Diesel engine emissions under fuel lean and fuel rich conditions was used. The model gas includes CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, NO, NO<sub>2</sub>, H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>. C<sub>3</sub>H<sub>6</sub> is used as model species for unburned hydrocarbons, simulating reactive unburned hydrocarbons such as olefins or aromatic hydrocarbons.

The gas compositions studied in this paper are given in Table 2.

**Table 2 – Model gas compositions. All measures are by volume.**

Species	Lean	Rich
NO	~200 ppm	~200 ppm
C <sub>3</sub> H <sub>6</sub>	0/60 ppm	60 ppm
CO	0/0.04 %	2.1 %
O <sub>2</sub>	12 %	0.9 %
CO <sub>2</sub>	7 %	7 %
H <sub>2</sub> O	10 %	10 %
H <sub>2</sub>	-	0/1%
N <sub>2</sub>	dilution	dilution
Temperature	250 °C	350 °C, 450 °C

The calculations are run transient until steady state is reached. The detailed surface reaction mechanism published by Koop and Deutschmann [3] is used for the calculations. This mechanism includes reaction steps for nitrogen oxide conversion, decomposition of hydrocarbons by hydrogen abstraction, oxidation of hydrocarbons by surface bound oxygen, oxidation of carbon monoxide to carbon dioxide and formation of water from hydroxyl adsorption. The model comprises 73 reactions among 22 surface and 11 gas phase species. All reactions are elementary except for oxidation of C<sub>3</sub>H<sub>4</sub> by surface bound oxygen, since the reaction paths of this process are unknown.

The parameters for overall efficiency and mass transfer were adjusted to the current system in Ref. [1], and model validation was performed. The values used are given in Table 3.

**Table 3 – Model parameters and settings**

Mass transfer factor	0.3
Overall reaction efficiency	0.2
Cell length, $\Delta x$	1 mm
Gas pressure	1 atm
Space velocity	40000 h <sup>-1</sup>
Inlet velocity	8 m/s (250 °C) 9.5 m/s (350 °C) 11.1 m/s (450 °C)
Void fraction	0.4
Washcoat thickness	0.1 mm
Effectiveness factor species	NO
Catalytic surface area per geometric surface area	25

### Results and Discussion

The effect of exhaust gas emissions on NO conversion in a NSC is studied by the use of flow analysis. The inhibition of NO oxidation by C<sub>3</sub>H<sub>6</sub> and CO under fuel lean conditions was studied, as well as H<sub>2</sub> acting as reducing agent under fuel rich conditions. Flow analysis is performed in the thin film layer at  $x = 10.25$  cm for all cases. Flow values are given in (mole/cm<sup>3</sup>.sec). A display limit of 1% of total flux is used if nothing else is stated.

### Lean phase

For the lean phase, the inhibition of CO and C<sub>3</sub>H<sub>6</sub> on NO oxidation is studied. CO and C<sub>3</sub>H<sub>6</sub> are introduced to the gas stream, and comparisons are made with the clean case (0% CO, 0 ppm, C<sub>3</sub>H<sub>6</sub>). NO mole fraction as function of distance is shown in Fig. 2 below. Experimental data is included when available.

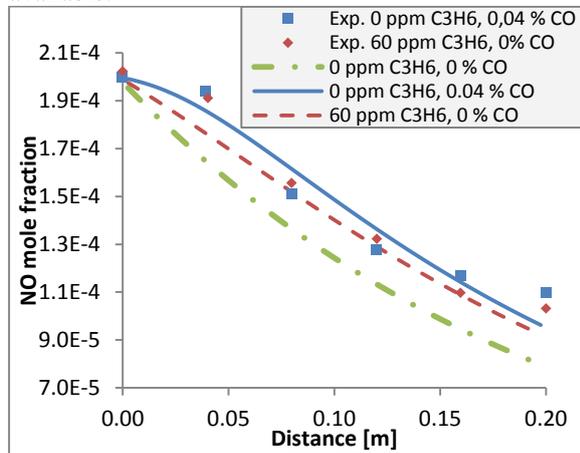


Figure 2 – The effect of C<sub>3</sub>H<sub>6</sub> and CO inhibition on NO oxidation under steady-state conditions in a flat-bed reactor. Gas composition: ~ 200ppm NO (according to experiment), 12% O<sub>2</sub>, 7% CO<sub>2</sub>, 10% H<sub>2</sub>O, balance N<sub>2</sub>. All measures are by volume. Temperature: 250 °C.

In Fig. 2 the inhibition of C<sub>3</sub>H<sub>6</sub> and CO is shown clearly; when any of these species are present in the exhaust gas, NO oxidation is decreased. In Ref. [1] surface site fractions were studied for variation of C<sub>3</sub>H<sub>6</sub>. C<sub>3</sub>H<sub>6</sub> was found to increase CO-Pt, introduce C<sub>3</sub>H<sub>5</sub>-Pt and decrease O-Pt, OH-Pt and active sites, Pt. From this information the following was concluded:

1. CO blocks active sites, hindering NO and oxygen adsorption, thus inhibiting NO oxidation.
2. CO-Pt decreases OH-Pt, which plays a role in NO oxidation; NO oxidation is further inhibited.
3. C<sub>3</sub>H<sub>6</sub> oxidation to CO-Pt is fast, leaving the more stable CO-Pt blocking the surface. The inhibition effect of C<sub>3</sub>H<sub>6</sub> should hence be very similar to that of CO.
4. Conversion of propene through reactions with surface bound oxygen is the fastest and major pathway. The H abstraction pathways via C<sub>3</sub>H<sub>6</sub>-Pt are slower.

The flow paths for nitrogen atoms are shown in Fig. 3 below. From this figure the following is deduced:

- The major pathway for NO oxidation is adsorption to oxygen sites, O-Pt, forming NO<sub>2</sub>-Pt. NO<sub>2</sub> is then desorbed.
- NO adsorption to active platina sites is weak under oxidizing conditions.
- NO oxidation follows the same pathways irrespective of CO and C<sub>3</sub>H<sub>6</sub> levels.

- NO oxidation is largest for 0.04% CO, and slowest for 60 ppm C<sub>3</sub>H<sub>6</sub>. This is confirmed by Fig. 3; the derivative of NO at x = 10.25 cm is highest for CO present in the stream, and lowest for C<sub>3</sub>H<sub>6</sub> present.

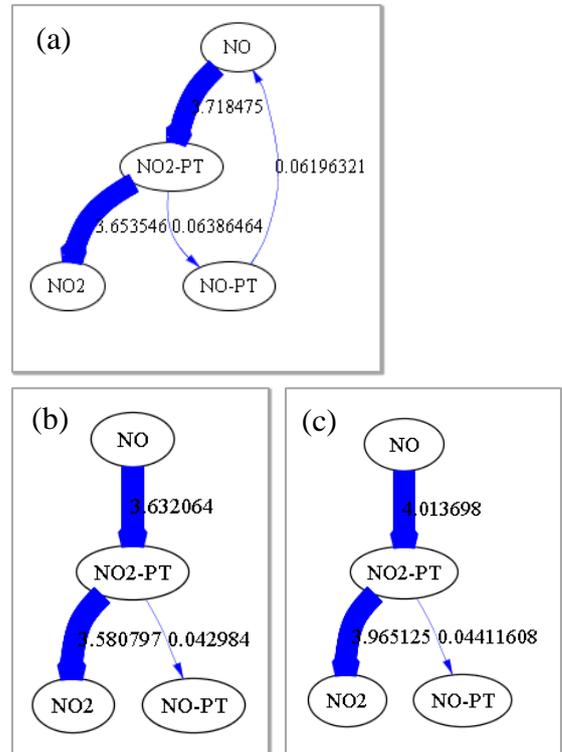


Figure 3 – Flow paths for nitrogen atoms, lean phase. (a) 0 ppm C<sub>3</sub>H<sub>6</sub>, 0% CO (b) 60 ppm C<sub>3</sub>H<sub>6</sub>, 0 % CO (c) 0 ppm C<sub>3</sub>H<sub>6</sub>, 0.04% CO.

Next the flow paths for carbon atoms are shown, in Fig. 4. Here it is seen that:

- The major pathway of C<sub>3</sub>H<sub>6</sub> is dissociative adsorption of C<sub>3</sub>H<sub>6</sub>, followed by oxidation down to C atoms. The H atom abstraction pathways via propylidin are slower. This confirms conclusion 4 in the list above.
- C<sub>3</sub>H<sub>6</sub> oxidizes to CO-Pt. The pathways from CO-Pt are identical with the CO oxidation pathways. This confirms conclusion 3 in the list above.
- The flow to C<sub>3</sub>H<sub>5</sub>-Pt ( $0.467 \frac{\text{mole}}{\text{cm}^3 \cdot \text{sec}}$ ) is greater than the flow from C<sub>3</sub>H<sub>5</sub>-Pt ( $0.446 \frac{\text{mole}}{\text{cm}^3 \cdot \text{sec}}$ ). This indicates C<sub>3</sub>H<sub>5</sub>-Pt accumulation. This is confirmed by the relatively high surface site fraction of C<sub>3</sub>H<sub>5</sub>-Pt, 5.65E-03, also noted in Ref. [1].

In Fig. 5 the oxygen atom flow for the case with C<sub>3</sub>H<sub>6</sub> present is shown. A strong competition for oxygen atoms is noted, which is the very reason to inhibition. Dissociative adsorption of NO competes with H, C and CO oxidation. Oxidation of NO-Pt by OH-Pt is not visible, since NO adsorption on Platinum sites is very weak. Thus the following

reaction path does not play any role for NO oxidation:  
 $\text{OH-Pt} + \text{NO-Pt} \rightleftharpoons \text{NO}_2\text{-Pt} + \text{H-Pt}$

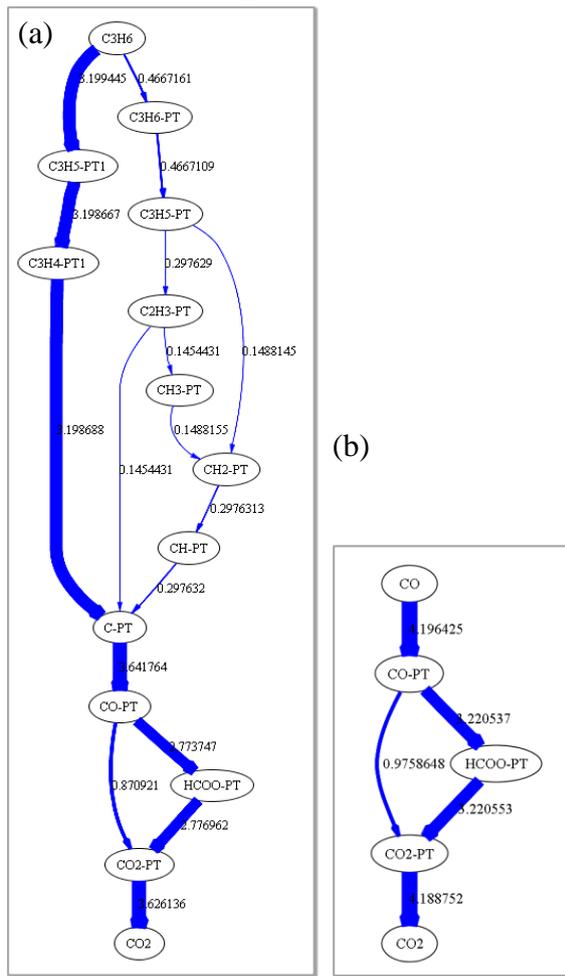


Figure 4 – Flow paths for carbon atoms, lean phase. (a) 60 ppm  $\text{C}_3\text{H}_6$ , 0% CO (b) 0 ppm  $\text{C}_3\text{H}_6$ , 0.04% CO.

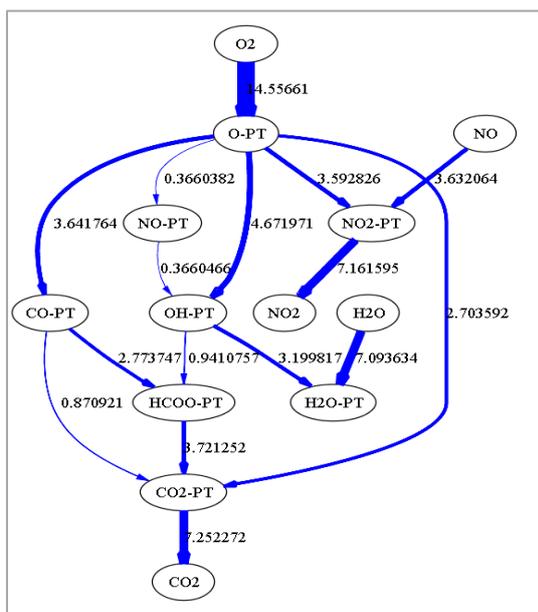


Figure 5 – Flow paths for oxygen atoms, lean phase. 60 ppm  $\text{C}_3\text{H}_6$ , 0% CO

This is contradictory to conclusion 2 in the list above. This shows the usability of flow paths for catalytic reactions; reaction paths and not only species fractions can be studied. The conclusion made based on reaction system and site fraction information only was proven to be incorrect.

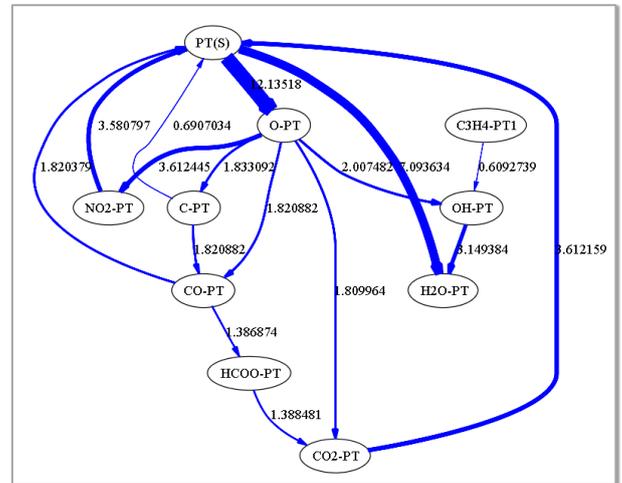


Figure 6 – Flow paths for platinum atoms for lean phase. 60 ppm  $\text{C}_3\text{H}_6$ , 0% CO

Finally the flow paths for platinum atoms at the surface are shown (Fig. 6). In this figure the competition for oxygen atoms and active sites is clear. This shows that conclusion 1 in the list above is partly correct; the inhibition is due to competition for active sites as well as competition for oxygen atoms.

#### Fuel rich phase

The effect of hydrogen as reducing agent for NO, and temperature dependence of NO conversion is studied for the fuel rich case. NO mole fraction as function of distance is shown in Fig. 7 below.

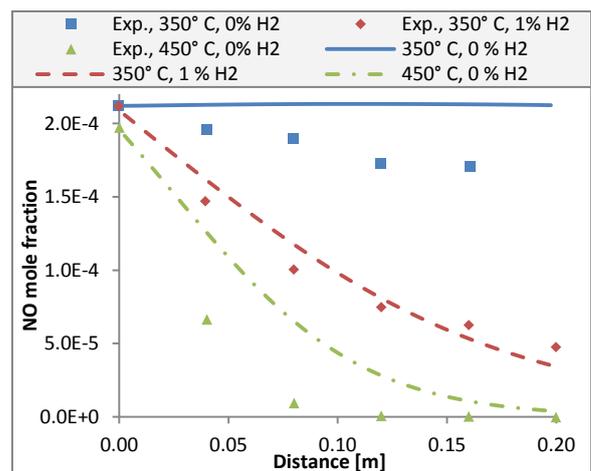


Figure 7 – The effect of  $\text{H}_2$  acting as reducing agent for NO under steady-state conditions in a flat-bed reactor. Gas composition: ~ 200ppm NO (according to experiment), 60 ppm  $\text{C}_3\text{H}_6$ , 2.1% CO, 0.9%  $\text{O}_2$ , 7%  $\text{CO}_2$ , 10%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$

The effect of H<sub>2</sub> acting as reducing agent is clear; For 350 °C, NO conversion is very slow without the presence of H<sub>2</sub>, and greatly enhanced by H<sub>2</sub>. At 450 °C NO conversion is significant even without hydrogen. The following conclusions were made in [1] about the system:

1. With hydrogen present, NO-Pt is reduced by H-Pt, forming OH-Pt and N-Pt.
2. At 450 °C free hydrogen atoms are formed from water decomposition at the surface. Thus NO reduction is possible even without H<sub>2</sub>, following the same pathways as for 350 °C with hydrogen.
3. The hydrogen oxidation pathways hinder the carbon monoxide pathways.

In Fig. 8 the flow paths for nitrogen atoms are shown for the cases where NO conversion is present. The pathways for NO reduction are identical, which is consistent with conclusion 2 above.

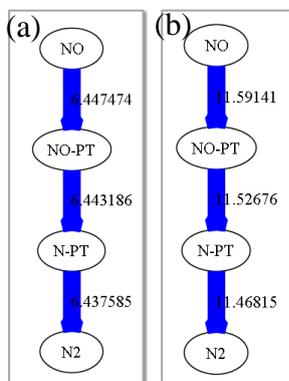


Figure 8 – Flow paths for nitrogen atoms, fuel rich phase. (a) 350 °C, 1% H<sub>2</sub> (b) 450 °C, 0% H<sub>2</sub>

In Fig. 9 the part of the flow paths for oxygen atoms related to NO reduction are shown.

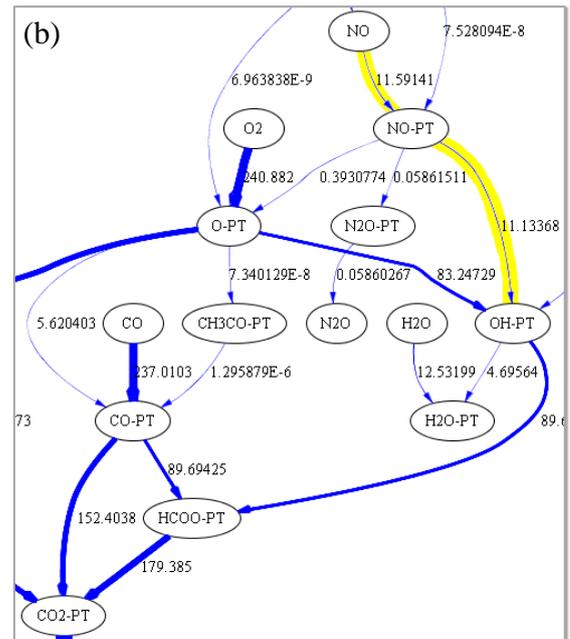
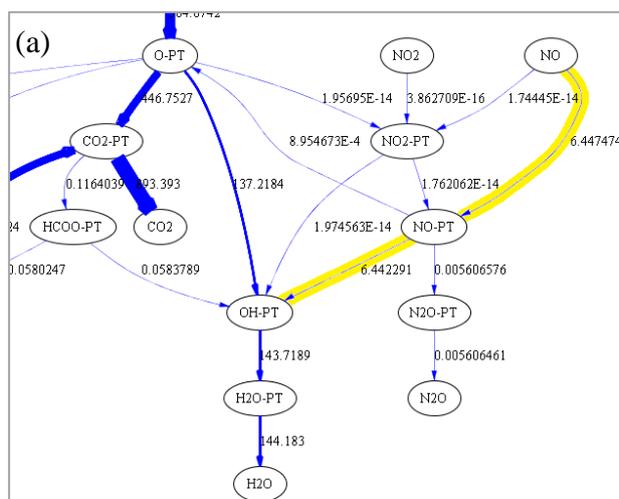
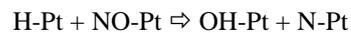


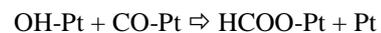
Figure 9 – Flow paths for oxygen atoms for fuel rich phase. (a) 350 °C, 1% H<sub>2</sub> (b) 450 °C, 0% H<sub>2</sub>. Display limit: 0% of total flux.

Fig. 9a shows a competition between H-Pt and CO-Pt for oxygen atoms. This confirms conclusion 3 above. It is also seen that NO is mainly reduced by H atoms, according to the following reaction (see the reaction paths marked with yellow in the figure):



This confirms conclusion 1 above.

The reaction path of OH-Pt differs between the cases; For 1% H<sub>2</sub> at 350 °C, OH-Pt reacts with H-Pt, forming H<sub>2</sub>O-Pt, which is desorbed. A net flow of oxygen atoms from NO to H<sub>2</sub>O is present. For 0% H<sub>2</sub> at 450 °C this reaction path is slow due to the lack of H-Pt. However, the following reaction is activated between 350 °C and 450 °C:



The reaction path is completed by H atom abstraction of HCOO-Pt, giving CO<sub>2</sub>, which is desorbed. Thus a net flow of oxygen atoms from NO to CO<sub>2</sub> is present, and H atoms are cycling between H-Pt, OH-Pt and HCOO-Pt.

In Fig. 10 the H atom flow paths are shown. In Fig. 10a the effect of H<sub>2</sub> acting as reducing agent is clear; Hydrogen dissociates at the surface, reduces NO and reacts with oxygen atoms to form OH, and further reacts with OH to form water.

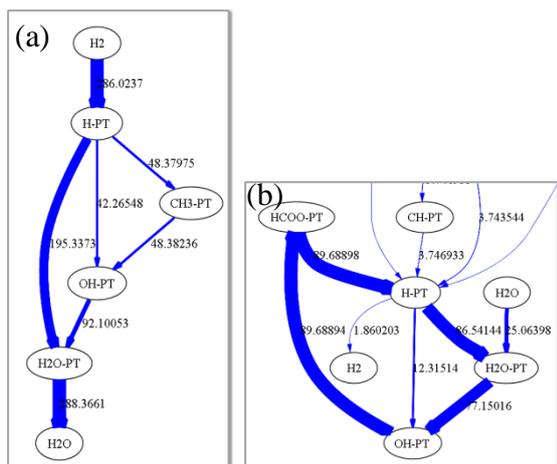


Figure 10 – Flow paths for hydrogen atoms for fuel rich phase. (a) 350 °C, 1% H<sub>2</sub> (b) 450 °C, 0% H<sub>2</sub>

In Fig. 10b the cycle of H atoms described above is clear. Furthermore, water is decomposed at the surface, yielding H atoms for this cycle. This is in consistence with conclusion 2 in the list above. In addition free hydrogen atoms are produced from hydrocarbon decomposition pathways (only partly shown in the picture for space requirements), which indicates even hydrocarbons can act as reducing agents. This was not noted in [1]. Interesting to note is also that gaseous H<sub>2</sub> is formed from H radicals, removing H radicals from the system. This is confirmed by the H<sub>2</sub> mole fraction; 35 ppm H<sub>2</sub> is formed in the channel.

## Conclusions

A transient 1D catalyst model was combined with heterogeneous flow analysis to study the reaction paths related to NO conversion in a Pt- $\gamma$ -alumina catalyst. Inhibition of NO oxidation by C<sub>3</sub>H<sub>6</sub> and CO was studied under lean conditions and the mechanism of H<sub>2</sub> acting as reducing agent for NO reduction was studied under fuel rich conditions. Conclusions made based on species fraction analysis in a separate publication [1] were scrutinized and confirmed / rejected:

### Fuel lean case

1. CO and C<sub>3</sub>H<sub>6</sub> inhibit NO oxidation by blocking active sites, and competing for oxygen atoms. In [1] the inhibition effect was addressed to site blocking only.
2. Under oxidizing conditions, NO is adsorbed to oxygen sites, forming NO<sub>2</sub>, which is then desorbed. Adsorption to active sites is weak.
3. The major oxidation pathway of C<sub>3</sub>H<sub>6</sub> is dissociative adsorption, followed by oxidation. The H atom abstraction pathways via C<sub>3</sub>H<sub>6</sub>-Pt are slower. This is consistent with the conclusions drawn in [1].
4. C<sub>3</sub>H<sub>6</sub> oxidizes to CO-Pt. The pathways from CO-Pt are identical with the CO oxidation pathways. This is consistent with the conclusions drawn in [1].

5. NO oxidation by OH-Pt is negligible since NO adsorption to active sites is weak. Thus the assumed correlation between OH-Pt and NO oxidation in [1] is rejected.

### Fuel rich case

6. H<sub>2</sub> reduces NO by the following reaction:  

$$\text{H-Pt} + \text{NO-Pt} \rightleftharpoons \text{OH-Pt} + \text{N-Pt}$$
 This is consistent with the conclusion in [1].
7. NO reduction pathways at 350° C with H<sub>2</sub> are identical to the pathways at 450° C without H<sub>2</sub>. This is consistent with the conclusions in [1].
8. At 350° C with H<sub>2</sub> present OH-Pt forms water, which is desorbed. A net flow of oxygen atoms from NO to H<sub>2</sub>O is present.
9. At 450° C the following reaction is activated:  

$$\text{OH-Pt} + \text{CO-Pt} \rightleftharpoons \text{HCOO-Pt} + \text{Pt}$$
 The pathway is completed by H atom abstraction giving CO<sub>2</sub>, which is desorbed. This yields a hydrogen cycle between H-Pt, OH-Pt and HCOO-Pt, enabling NO reduction even in the absence of H<sub>2</sub>. The net flow of oxygen is from NO to CO<sub>2</sub>. This was not found in [1].
10. At 450° C H<sub>2</sub>O dissociation and hydrocarbon oxidation are the sources of H atoms for the NO reduction cycle. Thus unburned hydrocarbons might act as reducing agents. This could not be seen by fraction analysis only in [1], where H<sub>2</sub>O dissociation was assumed to be the only source of H atoms.
11. At 450 °C H<sub>2</sub> is recombined and desorbed from the surface.

The conclusions above show that flow analysis is an efficient and valuable tool to understand catalytic processes, and can provide crucial information for development.

## References

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