

# Potassium in flame-made Pt/K/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> storage-reduction catalysts

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## Abstract

High surface area Pt/K/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared with a 2-nozzle flame spray method resulting in Pt clusters on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and amorphous K storage material as evidenced by Raman spectroscopy. The powders had a high NO<sub>x</sub> storage capacity and were regenerated fast in a model exhaust gas environment. From 300 to 400 °C no excess NO<sub>x</sub> was detected in the off gas during transition from fuel lean to fuel rich conditions, resulting in a highly effective NO<sub>x</sub> removal performance. Above 500 °C, the NSR activity was lost and not recovered at lower temperatures as K-compounds were partially crystallized on the catalyst.

## 1. Introduction

Stricter limits for exhaust emission motivate the development of new catalysts especially for NO<sub>x</sub> removal under oxygen rich conditions as encountered in lean burn and direct injection engines. NO<sub>x</sub> storage-reduction (NSR) catalysts [1] can trap exhaust NO<sub>x</sub> under fuel lean conditions on an alkali or alkaline-earth metal in the form of metal-nitrates. The alkalinity determines the NO<sub>x</sub> trap performance in the order: K > Ba > Sr ≥ Na > Ca > Li [2]. Regeneration of the NO<sub>x</sub> trap occurs under fuel rich conditions where metal-nitrates are decomposed and the released NO<sub>x</sub> is reduced to nitrogen [3]. Potassium- and barium-containing compounds have been studied extensively for their NO<sub>x</sub> storage capacity [4]. The best performance of K as storage

## 2. Experimental

The Pt/K/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the 2-nozzle FSP having an inter-nozzle distance (d) of 6 cm and an angle  $\varphi$  of 160° [5]. The NSR measurements were made with 20 mg of catalyst in a fixed-bed reactor (inner tube diameter of 4 mm). The NO<sub>x</sub> and NO concentrations in the effluent gas were monitored by a chemiluminescence detector (ECO Physics, CLD 822S).

The NO<sub>x</sub> conversion was measured at 250 – 600 °C while switching 50 times between oxidizing (3 min in 667 ppm NO and 3.3% O<sub>2</sub> in He) and reducing (1 min in 667 ppm NO and 1333 ppm C<sub>3</sub>H<sub>6</sub> in He) atmospheres. All catalysts were pretreated in 5% flowing H<sub>2</sub> for 10 min at the same temperature as the NO storage test was made. The total gas flow rate for all experiments was 60 mL/min corresponding to a space velocity of 72'000 h<sup>-1</sup>.

## 3. Results and Discussion

### 3.1 Structural properties

In XRD measurement only  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was detected [6] as the as-prepared K<sub>2</sub>CO<sub>3</sub> was amorphous and the Pt concentration was below the XRD detection limit. The Al<sub>2</sub>O<sub>3</sub> support was essential to produce high surface area powders (SSA = 146 m<sup>2</sup>/g) because the high surface area of pure Al<sub>2</sub>O<sub>3</sub> (SSA = 148 m<sup>2</sup>/g) keeps the K in a highly dispersed and amorphous state. Spraying only K precursor resulted in low surface, crystalline K<sub>2</sub>CO<sub>3</sub> with a measured SSA of 7 m<sup>2</sup>/g. The amorphous nature of the 2-FSP-made Pt/K/Al<sub>2</sub>O<sub>3</sub> was confirmed by Raman spectroscopy.

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### 3.2 *Dynamic NO storage-reduction*

The NO<sub>x</sub> conversion at different temperatures was measured for 50 fuel lean/rich cycles. The powder cycled very well at 300 °C with a NO<sub>x</sub> conversion above 80%. At 350 °C the NO<sub>x</sub> conversion was increased to 95% and at 400 °C almost no exhaust NO<sub>x</sub> could be detected at any time. At 500 and 600 °C the NO<sub>x</sub> conversion decreased for both catalysts to around 60%. This sudden drop could be attributed to partial crystallization of K<sub>2</sub>CO<sub>3</sub>, though no difference in XRD could be observed. After the test at 600 °C, the same catalysts were examined at 300 °C and had lost 50% of its performance compared to the corresponding fresh powder. This indicates that the initial structure of the Pt/K/Al<sub>2</sub>O<sub>3</sub> was altered at 600 °C and probably crystalline K<sub>2</sub>CO<sub>3</sub> was formed, similar as in the Raman investigation. Other catalysts were first cycled 50 times at 350 °C and subsequently cycled 50 times at 300 °C. The low-temperature aged catalysts showed similar, if not better, NO<sub>x</sub> conversions compared to a fresh catalyst at 300°C. To explain aging, further investigations are needed.

## 4. Conclusions

Flame synthesis of Pt/K/Al<sub>2</sub>O<sub>3</sub> resulted in amorphous K<sub>2</sub>CO<sub>3</sub> with NO<sub>x</sub> conversion >80% in the optimal temperature range of 300 – 400 °C. This high performance could be reached by fast NO<sub>x</sub> uptake during the fuel lean and fast regeneration during the fuel rich phase. Additionally the typical overshooting of the NO<sub>x</sub> signal during the switch from fuel lean to fuel rich gases was significantly decreased and never exceeded the inlet NO<sub>x</sub> concentration.

## 5. Acknowledgements

We thank for the financial support by ETH Zürich (TH-09 06-2) and the contribution of platinum chemicals by Johnson Matthey PLC is greatly appreciated.

## 6. References

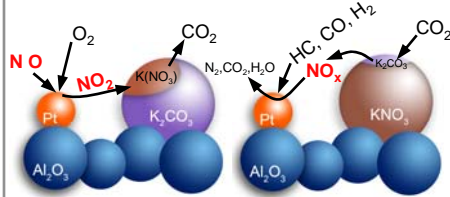
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## Objective

Pt/K/Al<sub>2</sub>O<sub>3</sub> catalyst can be used for abatement of combustion generated NO<sub>x</sub> in lean burn engines. Thereby effluent NO<sub>x</sub> is stored on K under oxygen rich conditions and is later regenerated during a short fuel rich period [1].

Here, catalyst powders were made using a two nozzle flame spray pyrolysis (FSP) setup. With this particle mixing as well as a preferential Pt deposition can be made by adjusting the precursor composition and geometry of the setup [2].



Simplified NSR working principle: On the left side NO<sub>x</sub> is stored during fuel lean condition and on the right side regenerated during fuel rich conditions

## Flame Synthesis



2-FSP setup to produce Pt/K/Al<sub>2</sub>O<sub>3</sub>: A liquid metal-organic precursor is dispersed and combusted. Flame made K- and Al component combine downstream.

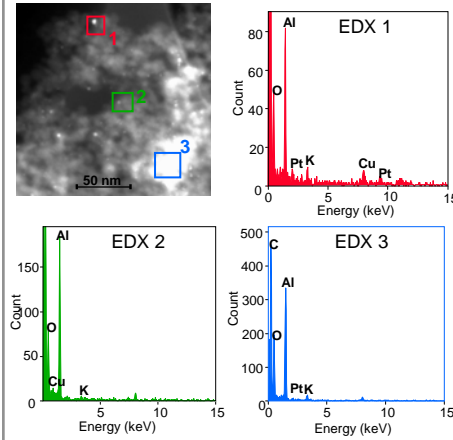
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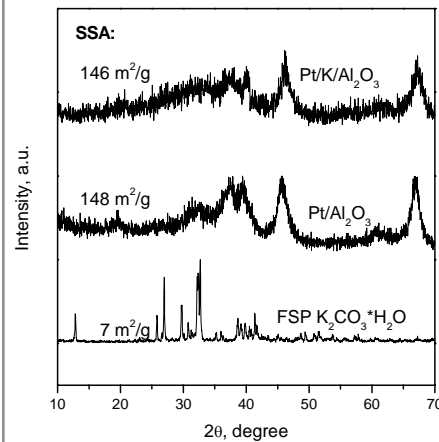
## Acknowledgements

We would like to thank Dr. Frank Krumeich from ETH Zürich for the electron microscopy analysis and kindly acknowledge financial support by ETH Zürich (ETH Research Grant TH-09 06-2). The contribution of platinum chemicals by Johnson Matthey PLC is greatly appreciated.

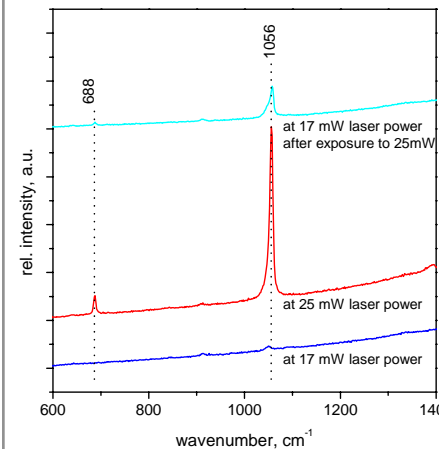
## Characterization



STEM with EDX show well distributed Pt, K and Al in the powder.

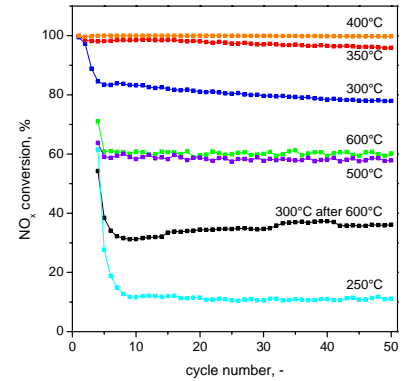


XRD of amorphous Pt/K/Al<sub>2</sub>O<sub>3</sub> compared to Pt/Al<sub>2</sub>O<sub>3</sub>. Al<sub>2</sub>O<sub>3</sub> support is needed, otherwise crystalline, low surface area K<sub>2</sub>CO<sub>3</sub> is formed.

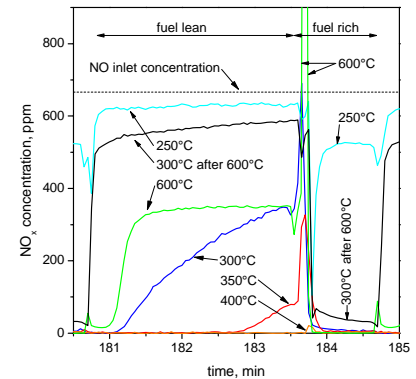


Raman spectroscopy of amorphous K. After high laser energy exposure the powder crystallizes and typical K<sub>2</sub>CO<sub>3</sub> Raman shifts can be observed

## Effect of cycling and operation temperature

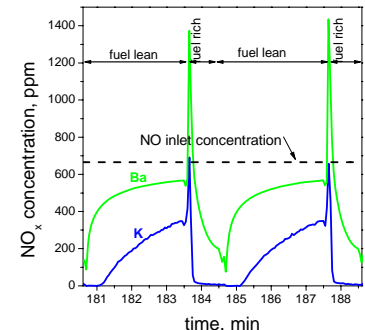


NO<sub>x</sub> conversion at different operation temperatures. Above 400°C the catalyst performance collapses and does not recover later at lower temperatures.



Outlet NO<sub>x</sub> concentration during the 48th cycle for different temperatures.

## Comparison K and Ba



Ba/Pt/Al<sub>2</sub>O<sub>3</sub> shows much higher break through NO<sub>x</sub> concentration compared to K/Pt/Al<sub>2</sub>O<sub>3</sub> during the switch from fuel lean to rich.

## Conclusions

Flame synthesis of Pt/K/Al<sub>2</sub>O<sub>3</sub> showed:

- NO<sub>x</sub> conversion >80% at 300 – 400 °C
- Temperatures above 500°C alter the catalyst structure lowering the catalyst performance.
- Reduced overshooting of NO<sub>x</sub>.
- This superior performance was attributed to good K distribution in the catalysts and the amorphous nature of the K species.