Two-nozzle flame synthesis of Pt/Ba/Al\textsubscript{2}O\textsubscript{3} for NO\textsubscript{x} storage

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ABSTRACT

NO\textsubscript{x} storage-reduction (NSR) is applied for exhaust gas treatment of lean fuel engines. The proximity between Pt and BaO in Pt/Ba/Al\textsubscript{2}O\textsubscript{3} NSR catalysts affect the storage-reduction due the different spillover length the different interaction with the support. Here, we applied a two-nozzle flame synthesis way to control the location of the deposition of platinum with Pt either on the alumina support or on the Ba storage component. Differently deposited Pt were elucidated by electron microscopy techniques. NSR behavior of these catalysts was investigated in a microreactor by switching between lean and rich conditions. Our studies on the effect of the preferential deposition of platinum on the alumina support or Ba storage component corroborate that the remote control of the different constituents is a crucial factor for high performance of NSR catalysts. Flame synthesis based on a two-nozzle system was shown to be a suitable tool for controlling the proximity of storage and reduction components in NSR catalysts.

Keywords: NO\textsubscript{x} storage-reduction catalysts, NSR, Flame spray pyrolysis, lean NO\textsubscript{x} trap

1 INTRODUCTION

NO\textsubscript{x} storage-reduction (NSR) is applied for exhaust gas treatment of lean fuel engines [1]. The proximity between Pt and BaO in Pt/Ba/Al\textsubscript{2}O\textsubscript{3} NSR catalysts has been found to affect the storage-reduction behavior due to its effect on spillover of NO\textsubscript{x} species[2]. Here we applied flame synthesis to control the location of deposition of platinum either on the alumina support (Figure 1) or on the Ba storage component (Figure 2). Pt on Al\textsubscript{2}O\textsubscript{3} is known for its good NO to NO\textsubscript{2} conversion. And NO\textsubscript{2} was shown to be stored best on the BaCO\textsubscript{3}. However, due the longer spillover this system has a disadvantage compared to Pt directly deposited on BaCO\textsubscript{3}.

For Pt in close contact with Ba (see Figure 2) the spillover distance is minimal. On the other hand the NO to NO\textsubscript{2} oxidation rate is expected to be lower and at temperatures around 600°C BaPtO\textsubscript{3} crystals can form reducing the catalytic activity [3].

2 EXPERIMENTAL

The Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalysts were prepared using a two-nozzle FSP set up as illustrated in Figure 3 with an angle \( \varphi \) of 160° between the two nozzles that results in mixing of the two flame plumes after 34 cm. A detailed description of the setup can be found in [4].
The specific surface area (SSA) of the as-prepared powders was measured by BET (Micrometrics Tristar). X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance instrument. The Pt dispersion was measured by CO-pulse chemisorption at 40°C on a Micromeritics Autochem II 2920 unit [5].

For scanning transmission electron microscopy (STEM), the catalyst material was dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid. The STEM images were obtained with a high-angle annular dark-field (HAADF) detector attached to a Tecnai 30F microscope (FEI; field emission cathode, operated at 300 kV), showing the metal particles with bright contrast (Z contrast).

The NO\textsubscript{x} storage-reduction (NSR) measurements were performed in a fixed-bed reactor. The reactor was allowing rapid switching between oxidizing and reducing conditions. The NO and NO\textsubscript{2} concentrations in the effluent gas were monitored using a chemiluminescence detector (ECO Physics, CLD 822S), and other gases were analyzed by means of a mass spectrometer (Thermostar, Pfeiffer Vacuum). NO\textsubscript{x} conversion for a full cycle (one storage and one reduction) was derived from following equation:

\[
\text{NO} \times \text{conversion} = \frac{\text{NO}_{\text{x,in}} - \text{NO}_{\text{x,out}}}{\text{NO}_{\text{x,in}}} \times 100\%
\] (1)

The NSR was measured at 300°C by switching 10 times between oxidizing (3 min in 667 ppm NO and 3.3% O\textsubscript{2} in He) and reducing atmospheres (1 min in 667 ppm NO, 1333 ppm C\textsubscript{3}H\textsubscript{6} in He). The total gas flow rate for all experiments was 60 mL/min.

3 RESULTS AND DISCUSSION

Preferential deposition of Pt on Al\textsubscript{2}O\textsubscript{3} (PtAl-Ba) or BaCO\textsubscript{3} (Al-BaPt) was made with the two-nozzle FSP setup as illustrated in Figure 3. The powders resulted in well mixed Pt/Ba/Al\textsubscript{2}O\textsubscript{3} mixtures as can be seen in Figure 4. The presence of Pt did not measurably influence the materials characteristics of γ-Al\textsubscript{2}O\textsubscript{3} or monoclinic BaCO\textsubscript{3} in all samples. After 2-3 weeks stored at ambient conditions the monoclinic BaCO\textsubscript{3} gradually transformed into thermodynamically more stable orthorhombic BaCO\textsubscript{3} [6]. The catalysts exhibited a specific surface area of 140 m\textsuperscript{2}/g and were non-porous. CO chemisorption showed CO/Pt molar ratios of 0.3 and 0.25 for PtAl-Ba respectively Al-BaPt. LA-ICP-MS measurements showed that the measured...
weight ratios Pt:Ba:Al₂O₃ was 1:21.3:100 corresponding very well to the prepared ratios of 1:20:100. It has been shown before that FSP made powders conserve the prepared weight ratios rather well [7].

Preferential deposition was confirmed by STEM analysis where Pt particles appeared as bright, spherical dots. In Figure 5 PtAl-Ba can be see how Pt particles are distributed on the alumina. In areas with high Ba content also some Pt particles can be seen there fore the separation is not complete as a small fraction of Pt particles eventually do not follow the main production stream or nucleate after the Al-Ba mixture. In Figure 6 the case with Pt on BaCO₃ (Al-BaPt) is shown. Not many Pt particles can be seen as Pt as well a as Ba appear wit similar brightness on STEM pictures.

In Figure 7 the NOₓ exhaust gas for a constant NO is plotted for the 4th cycle. The storage-reduction cycles of the three catalysts showed that the performance of PtAl-Ba is best in the beginning, whereas for the reduction (regeneration) Al-BaPt is superior and after 6 cycles it performs better than PtAl-Ba. PtAl-BaPt catalyst perform in between the two curves suggesting that the described effects are independent and can be seen as an other indicator for successful separation of Pt on BaCO₃ or Al₂O₃, respectively.

![Figure 7: NO storage for different position Pt/Ba/Al₂O₃ during the 4th cycle.](image)

### 4 CONCLUSIONS

Two nozzle flame spray pyrolysis is able to separate the position of Pt and produce Pt/Ba/Al₂O₃ catalysts with preferentially deposition of Pt on BaCO₃ and/or Al₂O₃. The storage-reduction cycling. The location of Pt deposition affected the stability and deactivation behavior of the catalysts as emerged from experiments where the catalysts where exposed to multiple storage-reduction cycling.

PtAl-Ba showed the highest NOₓ storage activity, however, NOₓ-conversion decreased for higher cycle numbers due to the insufficient regeneration of the Ba-nitrates at 300°C. Al-BaPt, on the other hand, maintained its original storage reduction performance under the given conditions.

### REFERENCES


