11th ETH-Conference on Combustion Generated Nanoparticles
August 13th -15th 2007

Two-nozzle flame synthesis of $Pt/Ba/Al_2O_3$ for NO_x storage

Robert Büchel[a,b], Reto Strobel[a,b], Alfons Baiker[b] and Sotiris E. Pratsinis[a]

[a]Particle Technology Laboratory, Sonneggstrasse 3, CH-8092 Zürich, ETH Zurich, Switzerland

[b]Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

---

A novel two-nozzle flame spray pyrolysis (FSP) process is presented for one-step preparation of $Pt/Ba/Al_2O_3$ particles as used for NO_x storage-reduction (NSR) catalysts. This material is of particular interest for engines operating under lean conditions for the NO_x abatement. According to the NSR concept, NO_x is stored under lean conditions in the form of alkali or alkaline-earth nitrates (in particular $Ba(NO_3)_2$) and reduced over a noble metal into N_2 during fuel rich periods.

Recently it has been shown that different Ba phases of impregnated materials strongly affect the NO_x storage capacity of $Pt/Ba/Al_2O_3$, and $BaCO_3$ decomposing at low temperatures (LT-$BaCO_3$) has been identified as the most active Ba species in the NO_x storage process.[1]

Flame aerosol and in particular flame spray technologies are versatile and continuous processes for production of a variety of ceramic nanoparticles.In contrast to spray pyrolysis, flame spray pyrolysis (FSP) is based on combustible precursor solutions, which provide the energy for the process.[2,3] A metal containing precursor solution is dispersed, ignited, and combusted. After evaporation and conversion of the metal precursor, particles are formed in the gas phase and supported noble metal catalysts (i.e., Pt/Al_2O_3) consisting of Pt particles (<5 nm) finely dispersed on Al_2O_3 particles (10-40 nm) have been made by FSP.

Compared to the conventional single-nozzle setup during FSP, the present stereoscopic two-nozzle setup adds further flexibility for the control of important flame parameters, such as temperature and concentration fields, that affect particle formation, and affords the control of particle mixing at the nano-level in multicomponent systems. The use of two separate nozzles, one as aluminum and the other as a barium/platinum source, resulted in individual Al_2O_3 and monoclinic $BaCO_3$ nanoparticles, exhibiting good NO_x storage activity. In contrast, using a single-nozzle process resulted in Al_2O_3 particles with amorphous Ba species with negligible NO_x storage capacity. Increasing the inter-nozzle distance resulted in late mixing of the two flame products and increased the amount of crystalline $BaCO_3$. At ambient conditions the as-prepared monoclinic $BaCO_3$ transformed into orthorhombic $BaCO_3$. Independent of the Ba loading, flame made nano-crystalline $BaCO_3$ showed a low thermal stability (decomposition below 900 °C, LT-$BaCO_3$) that was distinctly different from its “bulk” behavior (decomposition above 900 °C).

The synthesized materials were characterized by transmission electron microscopy, nitrogen adsorption, X-ray diffraction, and temperature programmed decomposition and tested for their NO_x storage behavior.

(1) Piacentini, M.; Maciejewski, M.; Baiker, A. *Appl. Catal., B* **2005**, *60*, 265.
(2) Pratsinis, S. E. *Prog. Energy Combust. Sci.* **1998**, *24*, 197.
(3) Mädler, L. *KONA* **2004**, *22*, 107.

Two-nozzle flame synthesis of $Pt/Ba/Al_2O_3$ for NO_x storage

R. Büchel[a,b], R. Strobel[a,b], A. Baiker[b], and S. E. Pratsinis[a]
[a]Particle Technology Laboratory, ETH Zurich, CH-8092 Zurich, Switzerland
[b]Institute for Chemical and Bioengineering, CH-8092 Zurich, Switzerland
buechel@ptl.mavt.ethz.ch www.ptl.ethz.ch

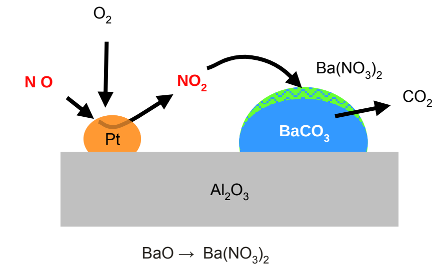
Objective

NO_x storage reduction (NSR) catalysts are used for abatement of NO_x from engines operating under lean conditions where conventional TWC catalysts are inefficient.
Here a flame process was used for synthesis of $Pt/Ba/Al_2O_3$ NSR-catalyst. Flame synthesis is a scaleable and continuous process for the synthesis of a variety of nano-particles, including noble metal catalysts. The two nozzle flame spray pyrolysis setup allows controlling particle mixing at the nano level in multicomponent systems. The structural properties of as-prepared materials were characterized and the catalyst have been tested for NO_x storage.

Working principle

Storage cycle

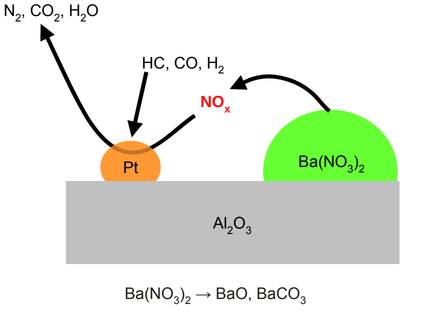
(fuel lean, oxidizing conditions)



During lean fuel condition effluent NO_x is stored in in the structure of alkali- or alkaline-earth nitrates, Here $BaCO_3$ is forming $Ba(NO_3)_2$. Additionally the noble metal catalyses the formation process.

Reduction cycle

(fuel rich, reducing conditions)

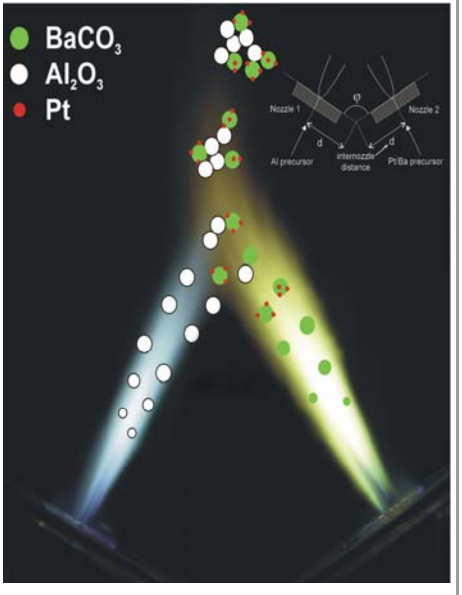


Is the capacity of the storage material exhausted the Ba will be regenerated using fuel rich conditions in the exhaust gas being provided by the engine or by extra fuel injection directly into the NSR catalyst

Acknowledgements

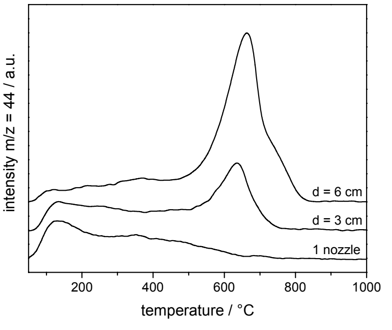
We would like to thank Dr. Frank Krumeich from ETH Zürich for the electron microscopy analysis and kindly acknowledge financial support by ETH Zürich (ETH Research Grant TH-2/03-2).

Setup

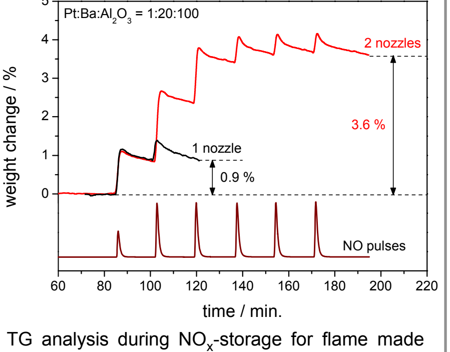


Two nozzle flame spray pyrolysis of $Pt/Ba/Al_2O_3$ where Al and Ba percursor solutions are sprayed in two separated FSP nozzles. After the formation of individual Al_2O_3 and $Pt/BaCO_3$ particles the two flames combine resulting in a well mixed powder.

Low Temperature $BaCO_3$



TPD CO_2 evolution profiles during decomposition of $BaCO_3$ for as prepared $Pt/Ba/Al_2O_3$ form one or two nozzles.

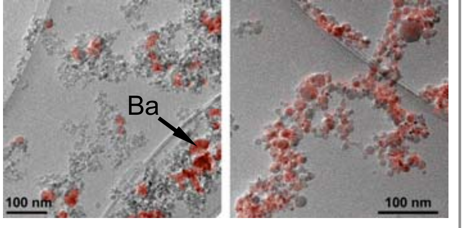


TG analysis during NO_x-storage for flame made $Pt/Ba/Al_2O_3$ made with one or two nozzles. NO pulses were injected into 5% O_2/He. In contrast to the two-nozzle made catalyst, only little NO was stored on the powder prepared with one nozzle.

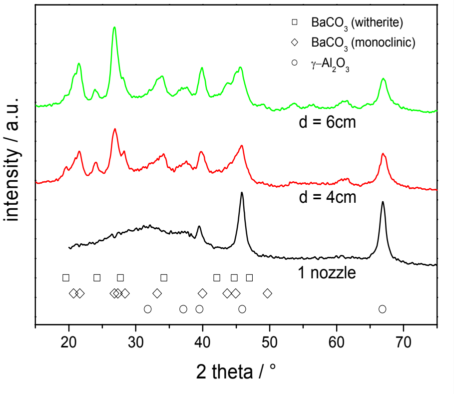
$BaCO_3$ morphology

2 Nozzles:
Separate Ba-particles

1 Nozzle:
Mixture of Ba-Al compounds



TEM images with corresponding Ba mappings (shown as a red overlay) for $Pt/Ba/Al_2O_3$ made with one and two nozzles. The used two nozzles resulted in the formation of individual $BaCO_3$ particles, whereas Ba is distributed all over the Al_2O_3 particles in the powder prepared with one nozzle.



XRD pattern of as-prepared $Pt/Ba/Al_2O_3$ made with one and two nozzles at different inter-nozzle distances. Increasing the inter nozzle distance resulted in higher amounts of crystalline $BaCO_3$: The initially formed monoclinic $BaCO_3$ phase transformed into the stable orthorhombic form within 4 weeks.

Conclusions

A novel two-nozzle flame spray pyrolysis (FSP) process was developed for one step synthesis of $BaCO_3$ and Al_2O_3 nanoparticles well-mixed at the nano level. The flame made $BaCO_3$ particles decomposed at low temperatures (LT-$BaCO_3$) compared bulk $BaCO_3$ particles (600°C vs 1000°C).
NO pulse experiments revealed no NO_x storage capacity for $Pt/Ba/Al_2O_3$ made with one nozzle, but good storage for catalyst made with 2 nozzles.

Further reading

R. Strobel *et al.*, Chem. Mater. 18 (2006) 2532.
R. Strobel *et al.*, Thermochim. Acta 445 (2006) 23.
M. Piacentini *et al.*, J. Catal. 243 (2006) 43.
R. Strobel *et al.*, J. Catal. 213 (2003) 296.
M. Piacentini *et al.*, Appl. Cat. B Environ. 60 (2005) 265.
M. Piacentini *et al.*, Top. catal. 30-31 (2004) 71.