A novel two-nozzle flame spray pyrolysis (FSP) process is presented for one-step preparation of Pt/Ba/Al$_2$O$_3$ 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$_2$O$_3$, 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$_2$O$_3$) consisting of Pt particles (<5 nm) finely dispersed on Al$_2$O$_3$ 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$_2$O$_3$ and monoclinic BaCO$_3$ nanoparticles, exhibiting good NO$_x$ storage activity. In contrast, using a single-nozzle process resulted in Al$_2$O$_3$ 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.

Two-nozzle flame synthesis of Pt/Ba/Al₂O₃ for NOₓ storage

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Objective

NOₓ storage reduction (NSR) catalysts are used for abatement of NOₓ from engines operating under lean conditions where conventional TWC catalysts are inefficient. Here a flame process was used for synthesis of Pt/Ba/Al₂O₃ NSR-catalyst. Flame synthesis is a scalable 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 NOₓ storage.

Working principle

Storage cycle (fuel lean, oxidizing conditions)

During lean fuel condition effluent NOₓ is stored in the structure of alkali- or alkaline-earth nitrates. Here BaCO₃ is forming Ba(NO₃)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.

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Setup

Two nozzle flame spray pyrolysis of Pt/Ba/Al₂O₃ where Al and Ba precursor solutions are sprayed in two separated FSP nozzles. After the formation of individual Al₂O₃ and Pt/BaCO₃ particles the two flames combine resulting in a well mixed powder.

Low Temperature BaCO₃

TPD CO₂ evolution profiles during decomposition of BaCO₃ for as prepared Pt/Ba/Al₂O₃ form one or two nozzles.

Conclusions

A novel two-nozzle flame spray pyrolysis (FSP) process was developed for one step synthesis of BaCO₃ and Al₂O₃ nanoparticles well-mixed at the nano level. The flame made BaCO₃ particles decomposed at low temperatures (LT-BaCO₃) compared bulk BaCO₃ particles (800°C vs 1000°C). NO pulse experiments revealed no NOₓ storage capacity for Pt/Ba/Al₂O₃ made with one nozzle, but good storage for catalyst made with 2 nozzles.

Further reading