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

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ABSTRACT

NO_x storage reduction (NSR) catalysts are applied for the abatement of NO_x from engines operating under lean conditions, where conventional TWC catalysts are inefficient. Here, a novel two-nozzle flame spray pyrolysis (FSP) process was developed for one-step synthesis of $Pt/Ba/Al_2O_3$ NSR catalysts, which conventionally are prepared by wet-phase processes. The use of two nozzles separating the formation of Al and Ba resulted in the formation of individual $BaCO_3$ and Al_2O_3 nanoparticles well-mixed at the nano level [1]. In contrast, amorphous Ba species dispersed over the Al_2O_3 particles were formed by the conventional single nozzle FSP process. NO pulse experiments revealed no NO_x storage capacity for $Pt/Ba/Al_2O_3$ made with one nozzle, but good storage on the catalysts made with two nozzles. In contrast to impregnated $Pt/Ba/Al_2O_3$, higher Ba loadings even increased the relative amount of Ba involved in the NO_x storage process. This can be attributed to the absence of HT-$BaCO_3$ in flame-made catalysts [2].

Keywords: flame synthesis, catalysis, nanoparticles, NOx storage reduction

1 INTRODUCTION

The $Pt/Ba/Al_2O_3$ material is of particular interest as NO_x storage-reduction catalyst (NSR) for engines operating under lean conditions [3, 4]. A decade ago, Toyota proposed the NO_x storage-reduction concept (NSR) for the NO_x abatement of lean-fuel engines [5]. 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 [6]. Generally these catalysts are prepared by wet impregnation of an alumina support from aqueous solutions of barium and platinum precursors [6]. 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, the so-called LT-$BaCO_3$ has been identified as the most active Ba species in the NO_x storage process [7, 8].

Flame aerosol and in particular flame spray technologies are versatile and continuous processes for production of a variety of ceramic nanoparticles [9-11]. Compared to the conventional single nozzle setup during FSP [11], 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 excellent control of particle mixing at the nano level in multicomponent systems. Here we show how a two-nozzle system can be beneficially used to control the structure of $Pt/Ba/Al_2O_3$ catalysts leading to enhanced NO_x storage behavior.

Structural properties and behavior in NO_x storage reduction is further compared to $Pt/Ba/Al_2O_3$ catalysts prepared by conventional impregnation technique.

2 EXPERIMENTAL

Figure 1 depicts the current two-nozzle flame spray pyrolysis setup. A combustible Al-precusor solution is fed into the left 2-phase spray nozzle (blue flame) whereas a combustible solution containing a Ba and Pt precursor is fed into the right nozzle (yellow flame).

Figure 1: Photograph of the two-nozzle FSP setup as used for preparation of $Pt/Ba/Al_2O_3$ catalysts. The Al and Ba particle streams are mixed after formation of individual Al_2O_3 and $BaCO_3$ nanoparticles.

Both precursor solutions were dispersed by oxygen and ignited by surrounding flamelets. After evaporation and burning of the precursor, particles are formed by nucleation, condensation, coalescence and coagulation. The position of mixing of Al and Ba particles was adjusted by varying the off-center distance (d) of the nozzles stereoscopically. The angle of the two nozzles was constant at 120°.

These flame-made catalysts were analyzed by X-ray diffraction, electron microscopy, nitrogen adsorption, temperature programmed decomposition, CO pulse chemisorption and CO-FTIR. Behavior during NO_x storage and reduction was measured thermo-gravimetrically by NO pulse technique [8] as well as in a fixed bed microreactor by switching between lean (667ppm NO, 6.67% O_2, 3 min) and rich (667ppm NO, 1334ppm C_3H_6, 1min) conditions. Structural properties and catalytic activity was compared to a standard impregnated $Pt/Ba/Al_2O_3$ catalyst [8].

3 RESULTS AND DISCUSSION

3.1 Structural Properties

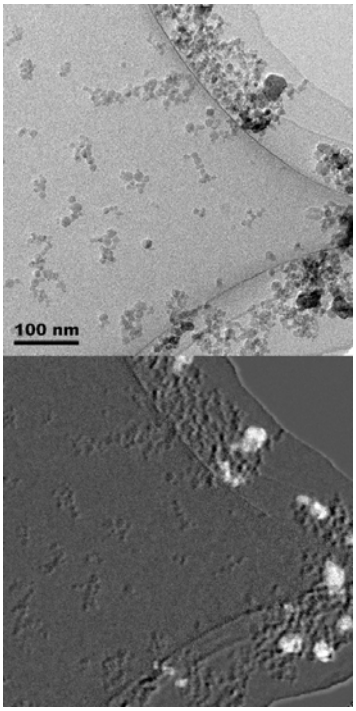

Figure 2: TEM images of $Pt/Ba/Al_2O_3$ prepared with two nozzles FSP. The corresponding mapping of Ba is shown as on the bottom

The applied two nozzle flame spray pyrolysis process resulted in the formation of individual Al_2O_3, $BaCO_3$ and Pt particles as desired for NSR catalysts. Figure 2 shows TEM images with corresponding elemental mappings of Ba for a catalyst prepared with two-nozzles or conventionally with one nozzle. It clearly shows the different distribution of Ba. The mixing of the two flame plumes after formation of Al_2O_3 and $BaCO_3$ particles resulted in a mixing of individual nanoparticles, whereas the one-nozzle process gave more a molecular mixing of Al and Ba species.

This distinct difference between one- and two-nozzle made catalysts is also revealed by measuring the amount of CO_2 evolved during thermal decomposition of $BaCO_3$. For the material prepared with one nozzle only evolution of CO_2 due to physically adsorbed CO_2 could be observed. In contrast by placing the two nozzles further away, or in other words mixing the two flames at a later stage during particle formation resulted in the formation of $BaCO_3$ as seen by CO_2 evolution above 500 °C. Adjusting the nozzle geometry allowed a precise control of the amount of $BaCO_3$ formed.

Figure 5 (left) shows the different species of $BaCO_3$ in flame-made and impregnated $Pt/BaCO_3$ /Al_2O_3 catalysts with different Ba loading. It has been found earlier, that there exist two different $BaCO_3$ species when dispersed on Al_2O_3. One is the so-called LT-$BaCO_3$ decomposing at low temperatures (< 900°C) the other behaves like bulk $BaCO_3$ and decomposes at temperatures above 900°C. In the flame-made catalysts only LT-$BaCO_3$ existed independent of the Ba loading, which stands in clear contrast to the buildup of HT-$BaCO_3$ in the impregnated catalysts at higher Ba loadings. This is an important difference as LT-$BaCO_3$ is the most active phase for NO_x storage as shown earlier.

3.2 Catalytic Behavior during NSR

The behavior during NO_x storage was measured thermogravimetrically by injecting NO-pulses in an O_2/He stream. Figure 3 shows the weight gain during these experiments for flame-made catalysts prepared with one and two nozzles. It clearly shows the very low storage capacity of the material prepared with one nozzle with only a very little weight gain due to stored NO_x. In contrast the catalyst prepared with two nozzles stored a significant amount of NO_x in the form of $Ba(NO_3)_2$.

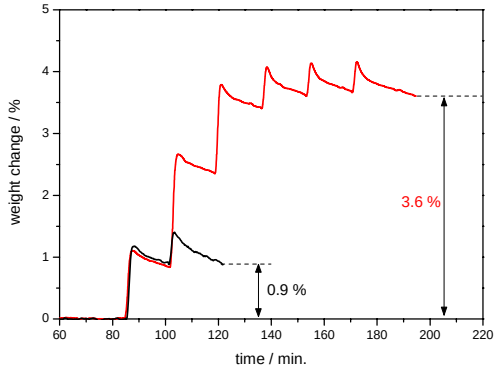

Figure 3: NO storage during NO pulse experiments on $Pt/Ba/Al_2O_3$ prepared with one and two nozzles. The weight increase reflects the amount of NO_x stored.

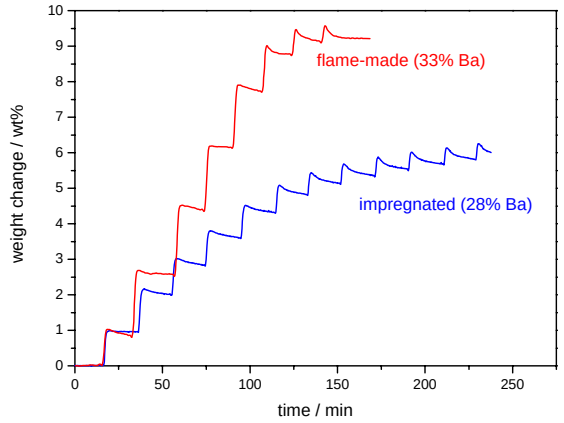

Figure 4: Weight increase during NO_x pulses on flame-made and impregnated $Pt/Ba/Al_2O_3$ catalysts.

Comparing now the catalysts with two nozzles to a standard impregnated catalyst revealed a much faster NO_x uptake for the flame-made catalysts. This is exemplarily shown in figure 4 for catalysts with a high Ba loading. Recalling now the presence of different $BaCO_3$ species in these catalysts (Fig. 6) clearly shows the advantage of the high amount of LT-$BaCO_3$ in the flame-made catalysts and confirms earlier observations. This is further reflected in the NO_x storage capacity of the catalysts taking into account the amount of Ba involved in the storage process. This has been determined by decomposition of the previously formed $Ba(NO_3)_2$ and measuring the amount of evolved NO. Figure 7 depicts the NO_x storage capacity for flame-made and impregnated catalysts as a function of the Ba-loading. In agreement with the formation of HT-$BaCO_3$ at high Ba loadings in the impregnated catalysts their NO_x storage capacity decreased at high Ba loadings whereas for the flame-made catalysts the NO_x storage capacity steadily increased with higher Ba loadings.

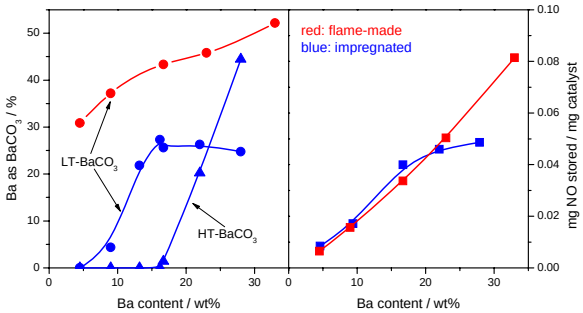

Figure 5: Comparison of different forms of BaCO3 (left) and amount of NO_x stored for flame-made and impregnated catalysts. At high Ba loadings an improved storage capacity was observed due to the absence of HT-$BaCO_3$.

Additionally NO_x storage and reduction was tested in a fixed bed reactor by switching several times between lean and rich conditions. Figure 6 shows a comparison of flame-made and impregnated catalysts. During the storage phase (first 3 min) there was no NO_x breakthrough in the flame-made catalysts whereas breakthrough of NO_x was observed on the impregnated catalysts. This is in agreement with the faster NO_x uptake in flame-made catalysts as discussed before. Figure 6 further shows that both catalysts were able to release and reduced the stored NO_x. Taking into account the storage and reduction phase the flame-made catalysts exhibited a higher NO_x conversion under the tested conditions.

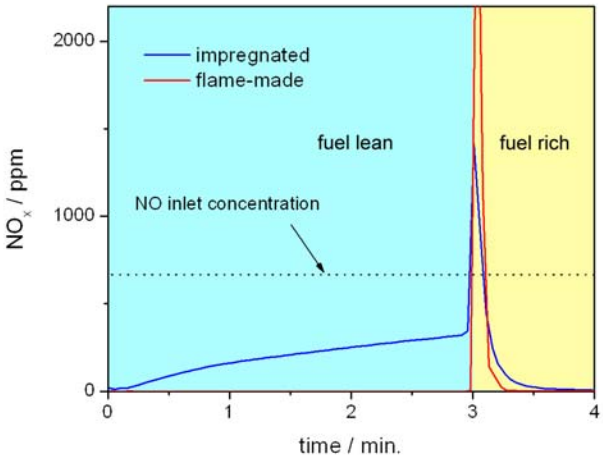

Figure 6: NO_x breakthrough during NSR on flame-made and impregnated catalysts during lean (3 min) rich (1 min) switches.

4 CONCLUSIONS

A novel two-nozzle flame spray pyrolysis (FSP) process was developed for one-step synthesis of $Pt/Ba/Al_2O_3$ consisting of individually crystalline $BaCO_3$ and Al_2O_3 nanoparticles well-mixed at the nano level. In contrast, amorphous Ba species dispersed over the Al_2O_3 particles were formed by the conventional single nozzle FSP process. The formation of individual $BaCO_3$ particles as achieved by the two-nozzle process was beneficial for the NO_x storage behavior, whereas no NO_x was stored on the single nozzle-made material. The amount of crystalline $BaCO_3$ could be controlled by varying the internozzle distance or in other words the point of mixing of the two flames. In contrast to impregnated catalysts, independent of the Ba loading the $BaCO_3$ nanoparticles decomposed at low temperatures (LT-$BaCO_3$) compared to bulk $BaCO_3$. This results in a faster NO_x uptake during the storage process, a higher NO_x storage capacity at high Ba loadings and a improved NO_x conversion during lean-rich NSR cycles.

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