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Flame synthesis of nanocrystalline ceria–zirconia: effect of carrier liquid

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Spraying cerium and zirconium precursors dissolved in carboxylic acids into a methane–oxygen flame resulted in well-structured nanocrystals of ceria–zirconia mixed oxides with high temperature stability and surface area.

The current generation of three-way catalysts for automotive exhaust gas treatment rely on ceria-zirconia as dynamic oxygen source for the conversion of remainders from incomplete combustion and the removal of NO. These mixed oxides have to withstand severe thermal stress in a rapidly changing exhaust gas atmosphere, and consequently tremendous effort is made to synthesize more stable materials.[1] High temperature preparations offer suitable methods for the manufacture of ceramics.[2] Therefore, several authors have attempted the preparation of ceria–zirconia by flame spray synthesis.[3] They obtained, however, inhomogeneous products with generally low specific surface area. Conventional wet-chemical mixed oxide preparation entails a series of process steps (precipitation, filtration, washing, drying and calcination) and produces large amounts of waste (salts from hydrolysis, washwater) while flame spray synthesis directly converts the carrier liquid containing the precursor solution into the ceramic nanoparticles.[4]

Here, we report the production of ceria–zirconia using a carboxylic acid derived carrier liquid that affords homogeneous and considerably smaller particles than reported before.† In flame spray synthesis, a liquid containing the desired metal oxide precursors is sprayed into a flame. Rapid droplet heating results in a complex precursor release into the gas phase where conversion to the oxides occurs. Diffusion controlled condensation results in small primary particles that further grow by collision and sintering. Segregation of constituents may occur by their different evaporation rates resulting in inhomogeneous powders. Several complex methods were investigated to overcome this problem, most are expensive (plasma assisted spray synthesis) or require high-cost precursors (organometallics, mixed alkoxides). Table 1 lists the surface areas of ceria–zirconia prepared by different methods. While precipitated materials exhibit reasonable stability at elevated temperature, demanding surfactant assisted precipitation must be applied to reach higher surface area. Flame spray made materials from ethanol or aminoglycols exhibit rather low surface area even before calcination.[3] Powders made by the procedure reported in this work have about 10 times higher surface area.

Fig. 1 (left) shows a high resolution transmission electron micrograph of the $Ce_{0.5}Zr_{0.5}O_2$. The high temperature gas-phase synthesis results in well-grown nanocrystals of ceria–zirconia with smooth surfaces. Crystals are not connected by sintering bridges. This morphology indicates a homogeneous distribution of the metal precursors in the gas phase. The carboxylic acid mixtures used in this work as carrier liquid offer a suitable way for fast delivery of the precursors to the flame. The fast heating of ceria–zirconia carboxylic acid salts is assumed to result in a sudden onset of decarboxylation. While CO_2 release in such salts starts around 250 °C, the simultaneously formed undecane (boiling point = 195 °C)–methane–CO_2 mixture exhibits an enormous pressure and triggers droplet explosion.[6] Fragments still containing carboxylic acids heat up even faster and further spread out in the flame. This mechanism agrees with the thermal decomposition mechanism of carboxylic acid salts of one electron oxidants such as Ce.[7] The amphiphilic character of the higher carboxylic acids and the preservation of electroneutrality within the liquid keeps the heavy metal ions well separated and favors high distribution.[8]

Fig. 1 (right) depicts a micrograph of $Ce_{0.5}Zr_{0.5}O_2$ after sintering at 900 °C for 2 h in air. Adjacent particles have grown together and formed regular sintering bridges. The overall structure, however, remains very open and few contacts between particles render sintering unfavorable thus corroborating the good thermal stability (Table 1). The production of mixed oxide nanoparticles in flames entails the problem of elemental segregation. Ill-defined precursor release by different volatility or decomposition pathways forms inhomogeneous products of reduced thermal stability. Fig. 2 compares the XRD patterns of two samples of $Ce_{0.7}Zr_{0.3}O_2$ prepared with different liquid carriers. The carrier composition applied previously by Mädler *et al.*[3a] forms a product containing a ceria rich (Fig. 2, left peak, bottom trace) and a zirconia-like phase (right peak). In contrast, application of the carboxylic acid based carrier solution used in this work results in a single mixed oxide phase (top trace). The precursor solution applied by Mädler *et al.* was based on iso-octane (bp = 99 °C), acetic acid (bp = 118 °C) and 2-butanol (bp = 99 °C). A droplet of this carrier mixture releases all liquid upon heating and a lump of the precursor salts remains, probably melts and decomposes. Different decomposition rates of the two metal precursors will then result in ceria or zirconia rich parts of the flame gas and particles of different

Table 1 Textural properties of ceria–zirconia mixed oxides prepared by wet-phase (precipitation) or high temperature flame spray synthesis

Preparation method	Ce content	BET area/m^2 g^{-1}	Calcination[a]	Reference
Precipitation	0.8	30	900 °C, 2 h	5[a]
Surfactant ass. precipitation	0.8	56	900 °C, 2 h	5
Surfactant ass. precipitation	0.68	40	900 °C, 2 h	5
Flame spray	0.1–0.9	10	As prepared	3
Flame spray	0.1–0.9	11–17	As prepared	3
Flame spray	0.1–0.9	130–170	As prepared	This work
Flame spray	0.7	68	900 °C, 2 h	This work
Flame spray	0.5	77	900 °C, 2 h	This work
Flame spray	0.3	82	900 °C, 2 h	This work

[a] Calcinations in air.

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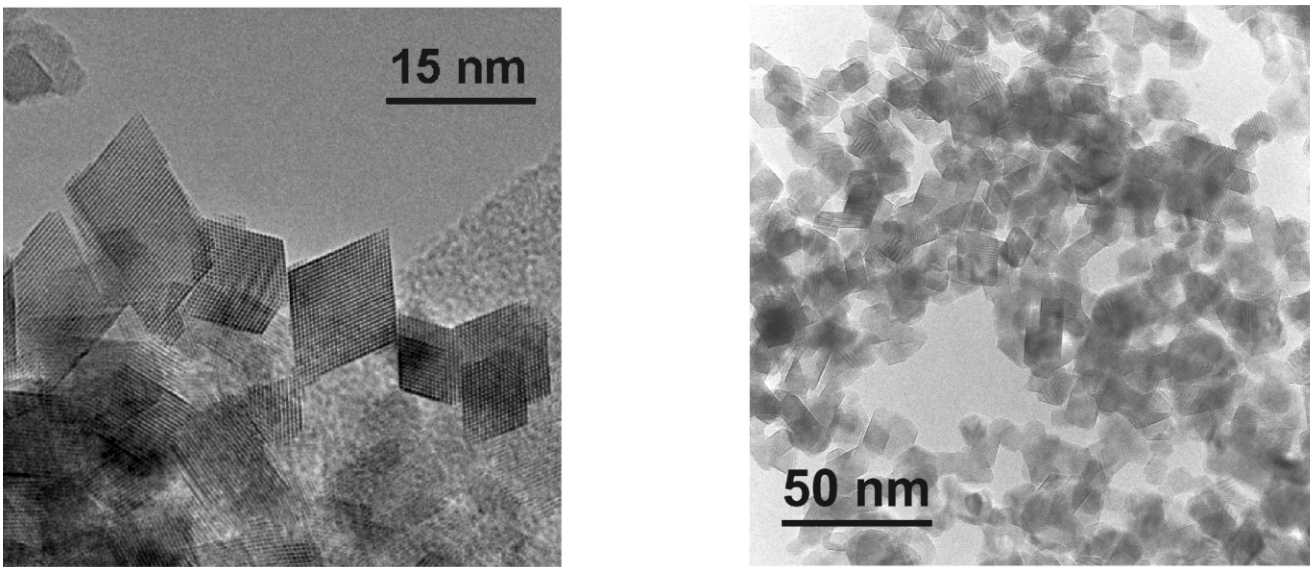

Fig. 1 Nanocrystals of $Ce_{0.5}Zr_{0.5}O_2$ as prepared (left) and after calcination (right). Lattice fringes indicate well developed single crystals in most cases. Calcination affords crystalline particles of similar size. Bridges stabilise free space between the crystals. The formation of the loosely interconnected network of bridged crystallites contributes to the thermal stability.

composition will be formed. Similar mechanisms are also conceivable in the ethanol based spray applied by Sutorik and Baliat.[3b] The carrier solution used by Laine *et al.*[3c] consisted of an aminoglycol. No reaction path leading to a sudden release of volatile compounds prior to the boiling temperature of the precursor allows good distribution of the precursor in the flame.[3]

To confirm the importance of precursor distribution, pure ceria was produced both by the low boiling iso-octane–acetic acid–2-butanol mixture and the here-described carboxylic acid based mixture (Table 2). Both produce ceria with similar surface, but calcination reveals a significant difference in thermal stability. Ceria produced with the acetic–lauric acid carrier is more resistant to textural changes induced by calcination. The present work clearly indicates that beside nozzle geometry, flame conditions and type of metal oxide precursor, the properties of the carrier liquid are a crucial parameter in determining the final morphological properties of mixed oxides prepared by flame spray synthesis.

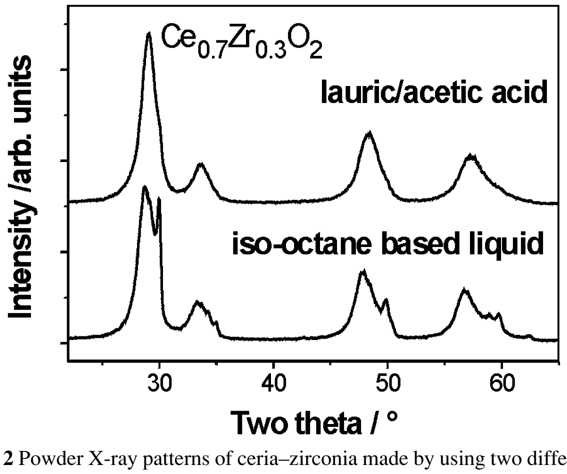

Fig. 2 Powder X-ray patterns of ceria–zirconia made by using two different liquid carriers for the precursors.

Table 2 Importance of liquid carrier in pure ceria production by flame spray pyrolysis and comparison to precipitated ceria

	Precipitated ceria[a]	Iso-octane–acetic acid–2-butanol[b]	Acetic–lauric acid[b]
As prepared	150 $m^2 g^{-1}$	174 $m^2 g^{-1}$	167 $m^2 g^{-1}$
900 °C, 2 h, air	8 $m^2 g^{-1}$	29 $m^2 g^{-1}$	39 $m^2 g^{-1}$

[a] Prepared according to [5a]. [b] Flame spray made.

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Notes and references

† Ceria–zirconia mixed oxide powders were produced by flame spray pyrolysis in a laboratory scale setup.[3a] Cerium(III) acetate hydrate (Aldrich, > 99.7%) and zirconium tetraacetylacetonate (Aldrich, 99%) were mixed according to the product composition and dissolved in a lauric–acetic acid (Fluka, > 99 %) mixture (1 : 1 by weight), heated to full dissolution resulting in a total metal concentration of 0.15 M.[4]

Solutions were delivered into the flame at 5 ml min^{-1} by a syringe pump (Inotec R 232) and atomized by 5 l min^{-1} oxygen (Pan Gas, 99.8%) dispersion gas. The flame consists of a central spray delivery (two-phase nozzle), a premixed, circular support flame (diameter 6 mm, slit width 10 μm) and a circular sheet gas delivery (ring of sinter metal, inner diameter 11 mm, outer diameter 18 mm). A mixture of methane (1.5 l min^{-1}, Pan Gas, 99%) and oxygen (3.2 l min^{-1}) was fed to the inner slit and formed the premixed flame. All gas flow rates were controlled by calibrated mass flow controllers (Bronkhorst EL-Flow F201). Powders were denoted as $Ce_xZr_{1-x}O_2$. Depending on composition, a production rate of 3.3 to 4.6 g h^{-1} was achieved.

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