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Short communication

Synthesis of TiO_2 core/RuO_2 shell particles using multistep ultrasonic spray pyrolysis

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ABSTRACT

Spherical submicron-particles with TiO_2 core–RuO_2 shell structure have been synthesized by employing sequential ultrasonic spray pyrolysis. The particles have been investigated by X-ray powder diffraction, scanning electron microscopy and different transmission electron microscopy techniques. The quality of the core–shell structure of the particles has been confirmed by comparison of the experimental data with those generated on the basis of a hard sphere core–shell model. It has been found that the mixing of the Ru-containing aerosol with the TiO_2 particle stream has a significant impact on the core–shell formation. The method introduced in this study can probably be applied for preparation of core–shell and core–multishell materials that are difficult to synthesize in a single step spray pyrolysis process.

1. Introduction

Systems that allow formation of core–shell particles by ultrasonic spray pyrolysis (USP) offer to alter the chemical composition and properties of core and shell by changing the process parameters. This allows tailoring of core–shell particles for specific applications. Because of its high catalytic activity and durability, the system RuO_2–TiO_2 is of interest for catalytic processes such as the oxidation of HCl. For the latter application Ramirez et al. report about a rutile type supported RuO_2 catalysts that is used in fixed bed reactors for chlorine recycling [1]. To improve the catalytic activity, it is desirable to use ultrafine particles composed of the binary metal oxides RuO_2 and TiO_2. To reach this goal, various approaches have been applied to prepare the oxide particles in this system [2–7]. Electrodes prepared by the sol–gel method exhibit a quite uniform and homogeneous distribution of the electrocatalytically active ruthenium spots [2]. In another study RuO_2–TiO_2 films have been deposited on float pearls using sol–gel-dipping method [5]. It was found that the TiO_2 has anatase structure, and that RuO_2 was highly dispersed within the formed material. However, this process yielded predominantly hollow spheres of a wide range of particle sizes between 10 and 100 μm. Supported RuO_2 catalysts were also obtained by incipient wetness impregnation of TiO_2 with aqueous solutions of $Ru(NO)(NO_3)_3{\cdot}xH_2O$ [6].

In the following we report on the synthesis of spherical RuO_2–TiO_2 submicron-particles with core–shell structure using a special variant of ultrasonic spray pyrolysis.

2. Experimental

Tetra-n-butylorthotitanate ($C_{16}H_{36}O_4Ti$), ruthenium (III) chloride hydrate ($RuCl_3{\cdot}H_2O$) and hydrochloric acid (HCl) were used as precursors for the synthesis of the RuO_2–TiO_2 particles. In contrast to conventional ultrasonic spray pyrolysis (USP) a modified set-up with separated ultrasonic atomizers for each precursor and two horizontal reactors for thermal decomposition was employed. According to the process chart in Fig. 1 titania particles are formed in the first pyrolysis zone from an aerosol containing tetra-n-butylorthotitanate.

The aerosol was generated with an ultrasonic frequency of 0.8 MHz. Pure oxygen was used as carrier gas at a flow rate of 1 l/min under atmospheric pressure. The second aerosol stream, generated at $f = 2.5$ MHz using a ruthenium (III) chloride hydrate precursor, was then admixed to the stream of solidified titania particles emerging from the first decomposition zone. This mixture was then piped through the second pyrolysis zone, where the desired core–shell particles were formed. In the last step

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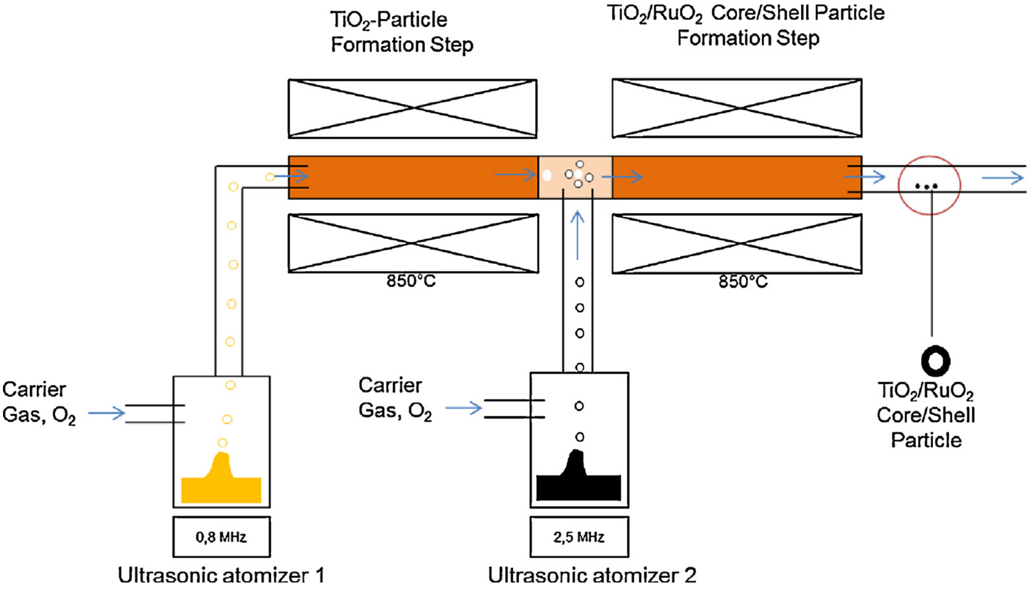

Fig. 1. Schematic set-up of two-step ultrasonic spray pyrolysis used for the synthesis of RuO_2–TiO_2 particles.

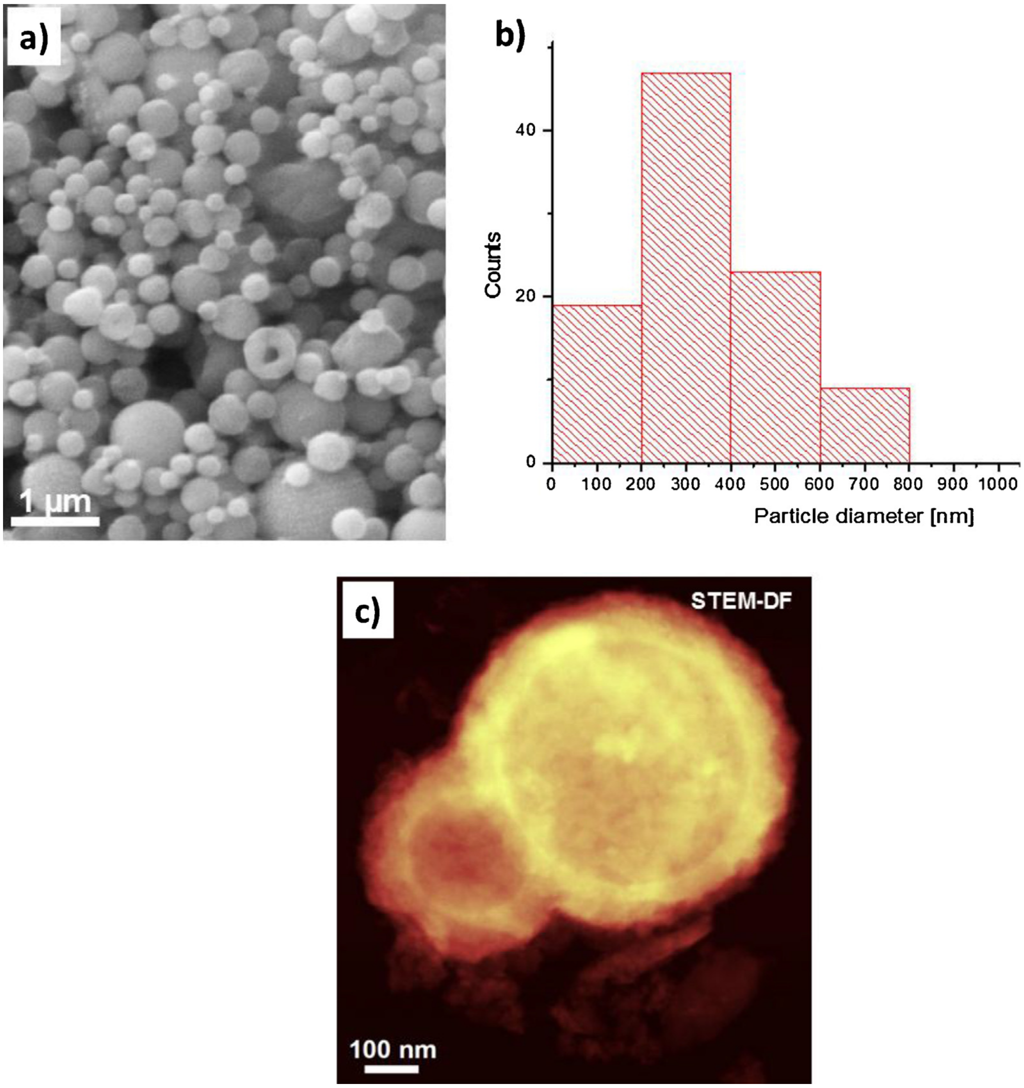

Fig. 2. (a) Typical particle morphology, (b) the size distribution and (c) HAADF (*Z*-contrast) image of RuO_2–TiO_2 core–shell particles synthesized at $T = 850\ ^\circ C$ using a molar Ru:Ti ratio of 1.0 ($f = 2.5$ MHz for Ru-based precursor, 0.8 MHz for Ti-based precursor). False colours have been used to enhance the core–shell structure of the particles.

the particles are separated from the carrier gas by passing the gas stream through a washing flask filled with water. The experiments were performed at decomposition temperature of 850 °C. The flow rate for both precursor materials was 1 ml/min. Initial characterization of the obtained particles was performed by powder X-ray diffraction (Philips PW1820) with Cu *K*α radiation and scanning electron microscopy (LEO1450VP) operated at 20 kV. For further characterization of the samples we employed high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDS) using a FEI Tecnai F20 operated at 200 kV. In addition to X-ray diffraction, selected area electron diffraction was used for phase identification of small volumes.

3. Results and discussion

Diffractograms obtained from the TiO_2–RuO_2 powders showed the presence of RuO_2 and TiO_2 in two different modifications: anatase and rutile. The semi-quantitative phase analysis was performed with the program X'pert HighScore Plus from PANalytical applying the Rietveld method. It was established that the amount of RuO_2-phase was 45 wt.%, rutile phase 40 wt.% and anatase phase 14 wt.%.

Analysis of the particles by SEM showed that nearly ideal spheres with mean particle diameters between 200 and 400 nm were formed during the sequential USP process (Fig. 2a and b). The size distribution was obtained by statistical analysis. Further investigation of the material by TEM proved that a substantial amount of the sample consists of submicron-particles with a core–shell structure (approximately 70% of core–shell particles) (Fig. 2c).

Phase identification performed on the basis of selected area electron diffraction (SAED) showed that the samples contain RuO_2 and TiO_2 with rutile structure. Additional peaks detected in some diffraction patterns also indicate the presence of TiO_2 in the anatase modification.

The core–shell structures were obtained for the smaller particles at a temperature of $T = 850\ ^{\circ}C$ and a molar Ru:Ti ratio of 1.0. The corresponding frequencies for the atomizers were $f = 2.5$ MHz for the Ru-based precursor and 0.8 MHz for the Ti-based precursor. The key that opened the window for synthesis of core–shell particles in this system was the mixing of the Ru-containing aerosol with the stream of titania particles from the first reactor. If the mixing of the particle stream with the aerosol is incomplete then we observed significant amounts of dense or hollow titania and mesoporous ruthenium oxide particles in addition to the desired core–shell material.

Analytical results such as EDX line profiles or element distribution maps from element spectroscopic imaging (ESI) are complex due to the special geometry of spherical nanoparticles. Thus the elemental profiles obtained from EDX (Fig. 3) were compared using a simple core–shell particle model, which is described in detail in [8].

In line with a previous investigation on core–shell particles in the Co/Co_xO_y system [8] it was assumed that the particles consist of a perfectly spherical core and shell with sharp interface separating the two phases. The line profile arising from the shell can be obtained by integration of the shell thickness along the vertical direction at each point. However, in order to match the profile with experimental data convolution with an instrumental broadening function becomes necessary. Comparison of the simulated trace of the shell with that obtained for ruthenium proves that the synthesized particles have indeed the desired core–shell structure. This result is also in agreement with the phase diagram for the RuO_2–TiO_2 system which contains neither a ternary phase nor a solid solution regime [9]. Moreover, due to the short residence time of the particles in the second reactor, which was estimated to be 2 s [10], interdiffusion of the core and the shell phase can be neglected.

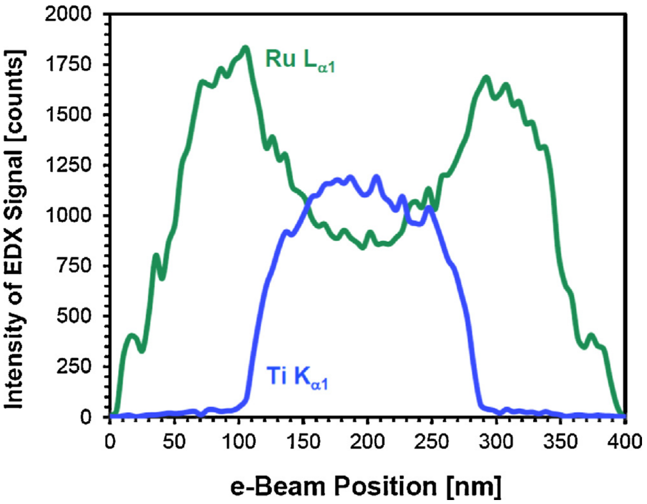

Fig. 3. EDX line scan across the core–shell particle. The trace of the separated elemental signals for ruthenium (Ru Lα1 line) and titanium (Ti Kα1 line) are in excellent agreement with the simulation for an ideal core–shell particle.

In order to obtain larger amounts of core–shell particles further modification of the process set-up is needed. A future development step should be especially focused on the optimization of the mixing device of the solid particle stream with the aerosol. In addition, operating conditions which would control the morphology, the particle size and the shell thickness need to be further investigated. This includes the most important parameters such as precursor concentration, temperature, carrier gas flow rates and residence time.

4. Conclusions

Spherical submicron-sized core–shell RuO_2–TiO_2 particles were prepared by a novel multi step variant of ultrasonic spray pyrolysis. Comparison of the results from TEM analysis with a hard-sphere model proved a core–shell structure of the particles. Further investigations will be directed towards process optimization in order to obtain tailored core–shell particles. It is believed that this approach is promising for the synthesis of different types of functional core–shell and core–multishell particles.

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