Direct synthesis of RuO_2/TiO_2 nanoparticles with core-and-shell structure for potential catalytic application

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Abstract

Ruthenium oxide (RuO_2) is a promising catalyst material for various industrially important chemical reactions, e.g. oxidation of hydrochloric acid. It has been shown that RuO_2, if deposited on a TiO_2 support, can act as an efficient electron transfer catalyst. The target of this study in the frame of DFG-SPP 1423 Program is to develop novel process designs of advanced RuO_2/TiO_2 nanocatalysts using the ultrasonic spray pyrolysis (USP). The use of USP for the synthesis of nanostructured RuO_2/TiO_2 particles from an organic metal salt-solution presents a completely new approach, because this complex catalytic system comprising both oxide support and active mass is obtained in one single step contrary to conventional procedures, which will be briefly reviewed in this paper. Products are predicted by thermochemical analysis using Software FactSage. The nanoparticle synthesis was performed at 800°C using different metal atomic fractions of tetra-n-butylorthotitanat and ruthenium (III) chloride hydrate in oxygen atmosphere. The degree of core-and shell structure formation was investigated using SEM, EDS, FIB, XREM, TEM, XRD analysis. The particle outer surface morphology was investigated by SEM, whereas the inner particle structure was studied by means of TEM and SEM carried out with crushed particles and particle cross sections obtained from focused ion beam (FIB) cutting. Furthermore, XRD analysis verified that the particles are at least partially crystallized. First information about the influence of the USP process parameters on the particle morphology was obtained by varying the atomic fractions of precursors and residence times in the synthesis.

Introduction

Because of good electrical conductivity and other properties ruthenium dioxide was tested as promising candidate for the catalyst in many industrial reactions. The catalytic activity of the surfaces of RuO_2 sets on at relatively low temperatures, leading potentially to massive savings in energy consumption during the operation of the catalyst for air purification. RuO_2 is an efficient hole and electron transfer catalyst on TiO_2 and seems to improve the efficiency of charge separation at the metal oxide/semiconductor interface, when deposited in small amounts, because an excess amount is capable of acting as a recombination centre. An important benefit of RuO_2 loading on TiO_2 is the increase of conductivity, which ultimately allows more efficient charge transfer within the photocatalyst in redox process. The scientists at the Berliner Fritz-Haber-Institute of the Max-Planck-Association and the Technical University in Vienna presented a model of RuO_2 (110) surface [Ove00], [Aßm04].

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The small ruthenium atoms are coordinatively unsaturated and have one atomic bond less than the bulk catalyst atoms. The unsaturated sites facilitate CO bonding and a subsequent reaction with oxygen.

Core-and-shell nanosized particles have attracted much attention because the free spaces are expected to be suitable for novel catalytic reaction. The preparation of RuO_2/TiO_2 was performed by different procedures [Col03], [Pan03], [Chu06], [Yao07], [Liu04]. They are generally prepared by thermal decomposition onto metallic titanium substrates. However, a variety of microanalytic studies have revealed that the surface composition and features of these electrodes are not homogenous. To clarify the physical properties of these electrocatalysts in detail and develop more extensive applications, it is desirable to obtain fine particles of binary metal oxides. In this regard, the sol-gel process is a good approach to prepare the oxide particles of this system. The advantage of using this technique is that one could find electrode structures which posses a uniform and homogeneous distribution of electrocatalytically active ruthenium points in all the electrode microstructure [Col03]. That feature cannot be obtained by the conventional decomposition method.

Panic et al. [Pan03] have prepared RuO_2/TiO_2 particles based on the sol-gel method. The oxide materials are in the form of the coating on titanium substrate as well as in the form of composites – high surface area carbon blacks impregnated with electrochemically active oxide. Their investigation included the examination of the oxide morphology and electrochemical behaviour, such as activity and stability in electrochemical reactions (chlorine evolution reaction and electro-organic synthesis) as well as pseudo-capacitive characteristics. The aim was to obtain an oxide material with high activity and stability, with good capacitive properties for potential application in electrochemical supercapacitors. The accelerated stability test showed that the oxide coatings prepared by the sol-gel procedure are more stable than the coatings prepared by thermal decomposition. This is due to the larger real surface area (smaller particles with narrow size distribution) of the sol-gel prepared coatings. Morphology, and consequently the electrochemical behaviour of sol-gel prepared coatings considerably depend on the conditions for oxide sols preparation, which was concluded by investigating the influence of the duration of forced hydrolysis for sol preparation, and the influence of the addition of alcohols into the dispersing medium of oxide sols on the electrode properties. The properties of sol-gel prepared RuO_2/TiO_2 coatings would be optimal if the RuO_2 particles were smaller and the TiO_2 particles were larger.

Chueh et al. [Chu06] have successfully prepared RuO_2/TiO_2 core-and-shell structure by reactive sputtering between 200°C and 500°C, at pressure 133.2 Pa and a radiofrequency power of 20 W. XRD spectrum of nanowires has shown that it is hard to distinguish if the individual peaks originate from either RuO_2 or TiO_2 owing to the fact that the lattice mismatch between RuO_2 and TiO_2 is less than 5 %. RuO_2/TiO_2 core-and-shell structure contains particles with diameter of 160 nm with a length of 1.5 µm. RuO_2/TiO_2 films were deposited on float pearls by the sol-gel-dipping method [Yao07]. The substrates were coated with RuO_2-TiO_2 precursor sol, air-dried at 120°C and further heated at 500°C to obtain the coupled photocatalyst of RuO_2/TiO_2 films supported on float pearls FP. The results showed that TiO_2 has anastase structure, and that the added RuO_2 was highly dispersed. It is found that the FP (the main components: SiO_2 and $Al_6Si_2O_3$) are almost hollow sphere with different particle sizes, and its diameter distribution lies between 10 and 100 µm. The film surface is smooth with the thickness of film about 1 µm (3 layers). Supported RuO_2 catalysts were prepared by incipient wetness impregnation of TiO_2 with aqueous solutions of $Ru(NO)(NO_3)_3$ x H_2O at 25 °C for 5 h [Liu04]. Impregnated supports were dried in ambient at 100 °C overnight and then in flowing dry air. Particle synthesis through USP method enable the generation of fine, submicronic to nanoscale, either single or complex, powders from a variety of precursor solutions [Gur09]. The process involves the formation of discrete droplets of precursor solution in aerosol form and the control over their thermally induced decomposition and phase transformation. Aerosol can be easily formed ultrasonically, using a high-frequency (100 kHz - 10 MHz) ultrasonic beam [Tsa04] directed to the gas-liquid interface. Liquid atomization and aerosol formation occur at a certain value of the acoustic waves amplitude, where the average droplet size depends mostly on the solution properties (viscosity, surface tension, concentration, density, etc.) as well as the ultrasound frequency. It was already shown for nanoparticle synthesis by Tsai et al. [Tsa04] that this technique is suitable for the aerosol formation with a narrow droplet size distribution. However, no information regarding to synthesis of nanocatalysts based on RuO_2/TiO_2 by ultrasonic spray pyrolysis USP is available to date. The main aim of this work is the synthesis of nanostructured RuO_2/TiO_2 particles from an organic metal salt-solution in one single step which presents a completely new approach, because this complex catalytic system comprising both oxide support and active mass are obtained from a common precursor.

Materials and Methods

Tetra-n-butylorthotitanat, ruthenium (III) chloride hydrate and hydrochloric acid were used as precursor for the synthesis of RuO_2/TiO_2 nanoparticles by ultrasonic spray pyrolysis. The most important parts of the set up are the ultrasonic atomizer, the reactor with three separated heating zones and an electrostatic precipitator. The temperature and pressure control was adjusted using a thermostat and a vacuum pump. Atomization of the obtained solution after dissolution of precursor took place in an ultrasonic atomizer (Gapusol 9001, RBI/ France) with one transducer to create the aerosol. Based on our previous results, the resonant frequency was selected to 2.5 MHz. Oxygen was flushed from bottle to oxidize ruthenium to ruthenium oxide continuously through the quartz tube in two different reactors: a) horizontal option (l= 0.3 m, d= 0.021 m, Fig. 1.a); b) vertical option (l= 1.5 m, b= 0.042 m; Fig. 1b) at a flow rate of 3 l/min. The calculated residence time in horizontal reactor at 800°C amounts about 0.2 s, what is more short in comparison to a value of 4.2 s in vertical reactor.

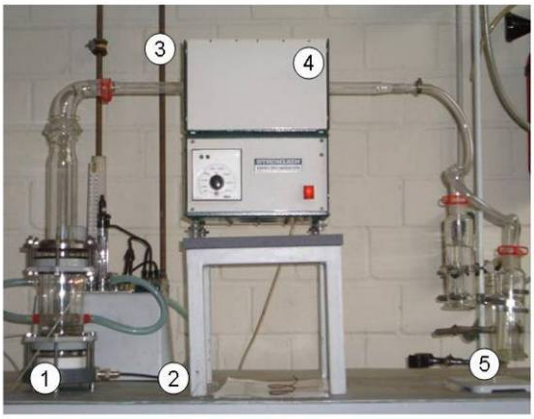

Fig. 1.a: Horizontal reactor

1. USP generator, 2. Thermostat, 3. Quartz tube, 4. Furnace, 5. Collection of powder

Fig. 1.b: Vertical reactor

Then atomized droplets of the solution based on Ru and Ti in an ultrasonic generator are further transported by oxygen to the furnace (vertical and horizontal reactor). After thermal decomposition of transported aerosol in the furnace, the Ru-Ti based nanopowder were collected in a reaction tube (Fig. 1.a) and an electrostatic field (Fig. 1.b).

XRPD analysis of the nano-sized sample powders was performed with a Bruker D8 Advance Diffractometer utilizing Bragg-Brentano Geometry and $\theta-\theta$ synchronization of both the X-ray tube and the detector. The X-rays were produced with a Cu-anode. For the detection of the diffracted X-Rays, the lithium drifted silicon "Sol-X Energy Dispersive X-Ray Detector" was used. The intensity contributions of both Cu $K\alpha_1$ (λ=1.5406 A) and Cu $K\alpha_2$ (λ=1.54439 A) radiation were recorded, whereas contributions of K-ßs are removed from the spectrum. The generator voltage was 40 kV and the current is set to 40 nA. Different molar ratios of Ru and Ti (0.333; 0.222; 0.166) were tested at 800°C in oxygen atmosphere in order to analyse a formation of core-and-shell structure. A scanning electron microscope ZEISS DSM 962 (1994) with W-cathode (lateral resolution 2.5 nm at 30 kV) was used for the characterization of the obtained RuO_2/TiO_2 powders.

SEM images were used to observe the surface morphology of particles formed at different parameter sets. An estimation of the impurity level was performed by energy disperse spectroscopy (EDS) analysis with a Si(Bi) X ray detector, connected with the SEM and a multi-channel analyzer. An EDX-System Oxford Link ISIS with HPGe-Detector and UT-Window was used for chemical analysis of microscopic volumes for all elements with atomic number > 4. The imaging and analysis of very fine particles was performed by transmission electron microscopy analysis using FEI Technai F20.

The electrostatic precipitator used a high voltage device by Eltex, Elektrostatik-GmbH, Weil am Rhein, Germany to enable the collection of the nanopowder in a special constructed quartz tube.

Results and Discussion

Thermodynamic consideration

Phase equlibria in RuO_2/TiO_2 system by Hrovath et al. [Hro93] was studied up to 1400°C. Preliminary results indicate the existence of solid solubilities at 1300°C of approximately 8 % RuO_2 in TiO_2 and a little over 10 % TiO_2 in RuO_2. At 1400°C RuO_2 decomposes to Ru and oxygen. Below a temperature 1400°C it is present one mixture of RuO_2 in TiO_2. The software FactSage was used to calculate the stability limits of RuO_2 and TiO_2 in dependence of gas partial pressure.

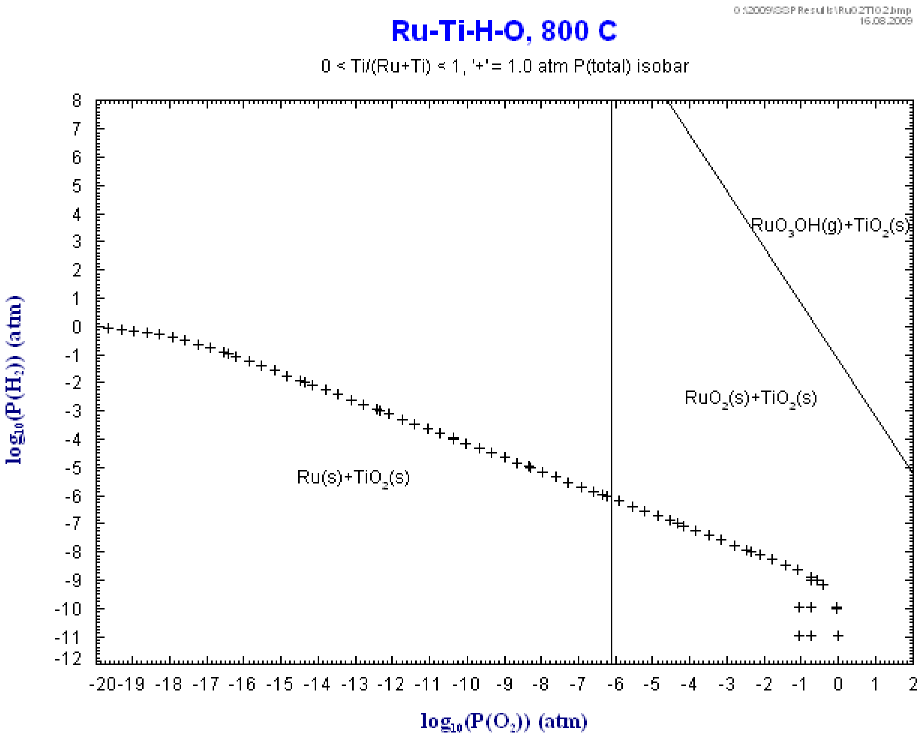

Fig. 2: Stability of RuO_2 and TiO_2 at 800°C dependently on partial pressure of oxygen and hydrogen

X-ray Analysis

Rietveld analysis has shown the following components in obtained RuO_2 /TiO_2 powder.

Table 1: Rietveld analysis of obtained powder

Molar ratio of Ru and Ti:	Anatase TiO_2 (%)	Rutile TiO_2 (%)	RuO_2 (%)
0.333	5.11	63.79	31.1
0.222	-	16.35	83.65
0.166	-	87.81	12.19

Characterisation of obtained powders

TEM carried out on a lamella cut by means of a focused ion beam (FIB) technique revealed that RuO_2/TiO_2 particles prepared in a horizontal reactor (T=800°C, ratio 0.333; f=2.5 MHz, oxygen flow rate 3l/min) partially exhibited a core and shell structure (shown in Fig. 3, right image).

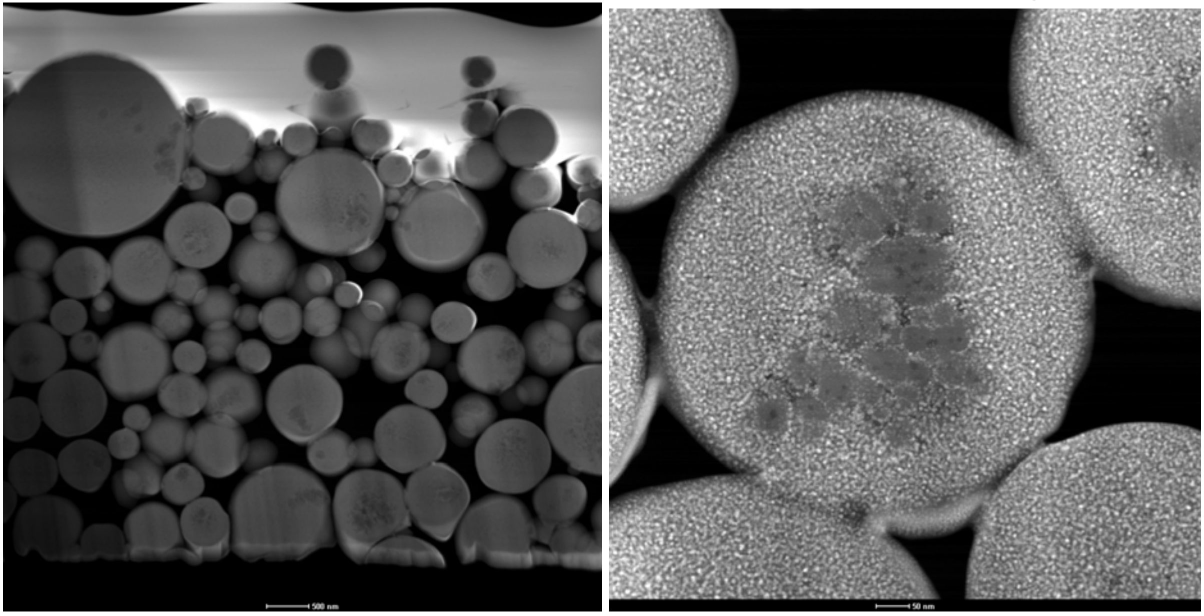

Fig. 3: FIB and SEM analysis of obtained powder (T=800°C, ratio 0.333; f=2.5 MHz, horizontal reactor)

The dark areas indicate the TiO_2 core, which consists of several sub-particles, each of which is decorated by Ruthenium-rich particles of the size of 1-5 nm (Fig. 4). EDS analysis of the dark areas confirmed a high titanium concentration, but also the presence of Ru.

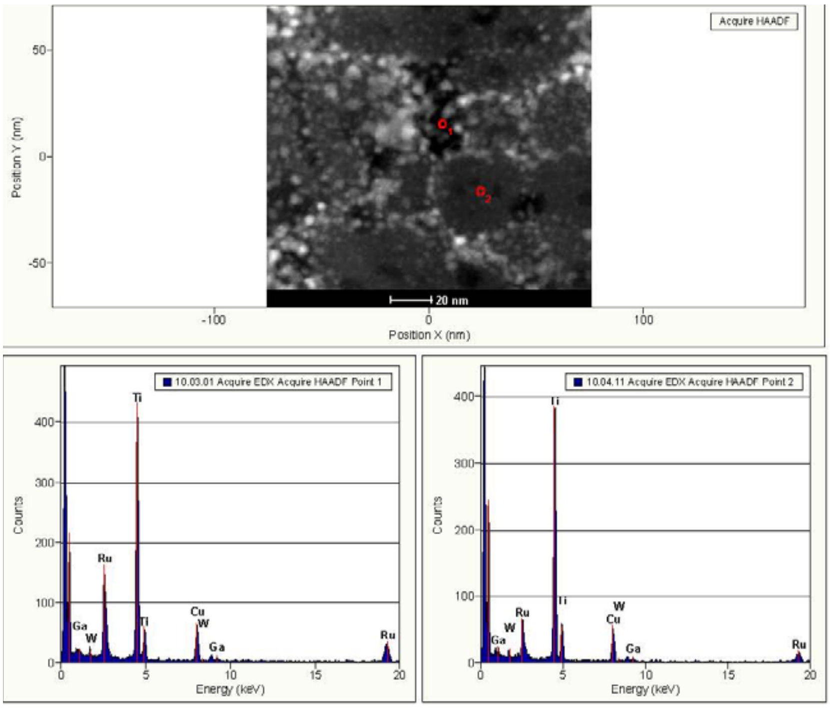

Fig. 4: Small separated nanoparticles with core-shell structure

Due to the short residence time in the horizontal reactor (Fig. 1.a) new experiments were performed in a vertical reactor (Fig. 1.b). TEM analysis of the powder obtained at 800°C, ratio Ru:Ti of 0.333, frequency of 2.5 MHz is below shown (Fig. 5 and Fig. 6)

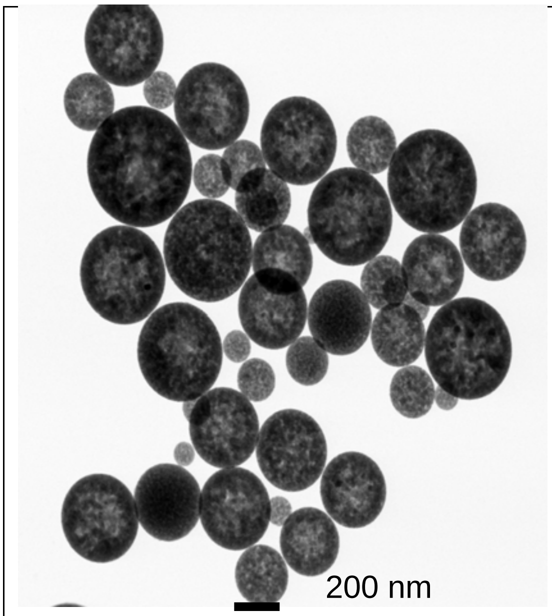

Fig. 5.a. TEM analysis

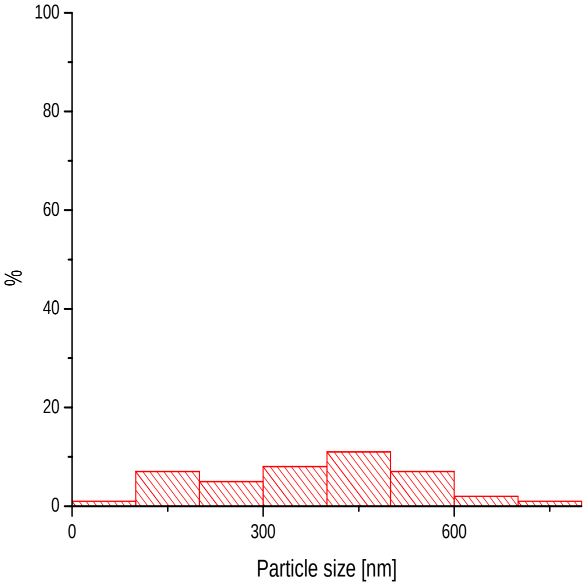

Fig. 5.b. Particle size distribution

The obtained particles are spherical with different sizes up to 700 nm (Fig. 5.b).

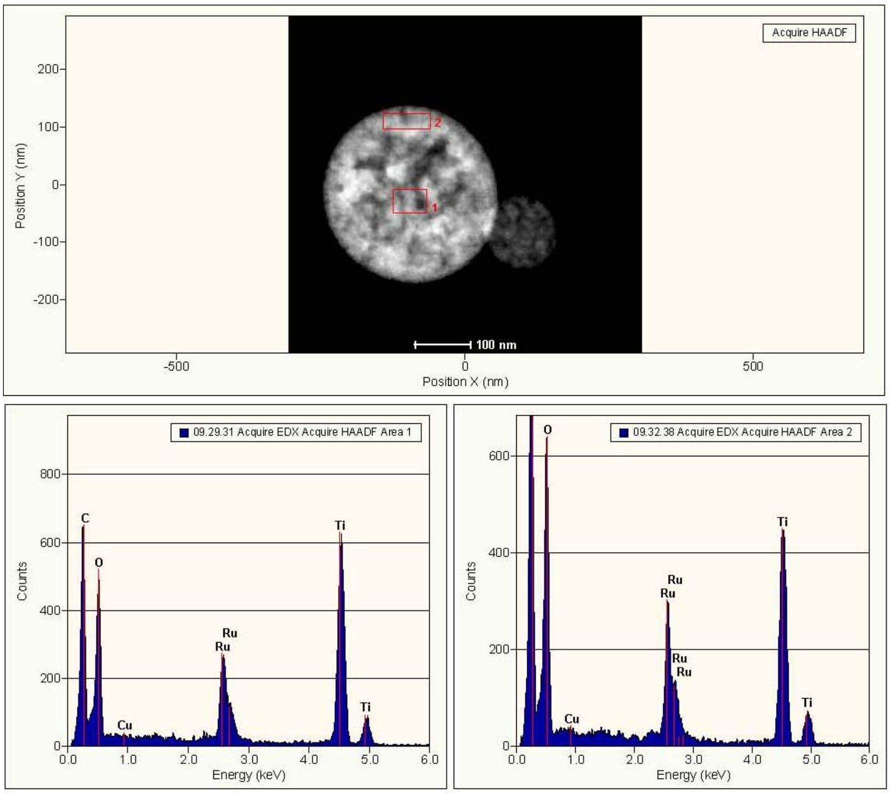

Fig. 6: High Angle Annular Dark Field HAADF detection of nanosized particles

As shown in Fig. 6, the majority of the core consists of TiO_2, while the shell is predominately composed of RuO_2. Atomic fractions of precursors, solvent type and process temperature play a crucial role in the formation of core-and-shell structures of Ru-Ni [Den08], which shall be tested in our future work related to RuO_2/TiO_2.

Conclusion

Phase equilibria in RuO_2/TiO_2 system was considered in order to predict final products. Spherical nano-sized RuO_2/TiO_2 with core-and-shell structure were prepared in a single step spray pyrolysis process as potential candidate for a catalytic application. The influence of the atomic ratios of ruthenium and titanium in precursor and reaction temperature on core-and-shell structure will be in next paper discussed.

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