# Process design of ultrasonic spray pyrolysis synthesis of $Ru/TiO_2$ nanoparticles

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**Abstract**

The use of USP for the synthesis of nanostructured $Ru/TiO_2$ particles from an organic metal salt-solution was shown a completely new approach, because this complex catalytic system comprising both metal support and active mass were obtained in one single step contrary to conventional procedures. Products are predicted by thermochemical analysis using Software FactSage under different atmosphere.

## Introduction

The target of this study in the frame of DFG-SPP 1423 Program was to develop novel process designs of advanced $Ru/TiO_2$ nanocatalysts using the ultrasonic spray pyrolysis USP method. The use of USP for the synthesis of nanostructured $Ru/TiO_2$ particles from an aqueous or organic metal salt-solution is a completely new approach, because this complex catalytic system comprising both metal support and active mass will be obtained in one single step contrary to conventional procedures [1-4]. This innovative route allows a better control of the process and final powder, reduces waste formation and simplifies the catalyst present manufacturing method. Due to an increased surface-to-volume ratio, nanostructured catalysts are expected to be extremely effective and accelerate the oxidation reactions. A high stability of nanocatalyst under reaction conditions is expected what leads decreased material costs. By addressing the complex problems faced by the aerosol synthesis procedures, this work aims to make a significant contribution for a better understanding of the synthesis of high quality nanostructured catalysts having well controlled morphology. With regards to that, two subjects were considered: a) Thermochemical modeling of the synthesis in order to understand the influence of precursor solution on the nanoparticle formation, b) Determination of the most impacting parameters in this single-step USP process for $Ru/TiO_2$ synthesis.

## Materials and Methods

Tetra-n-butilorthotitanat, 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 part 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. Regarding to our previous results the resonant frequency was selected to 2.5 MHz. Nitrogen was flushed from bottle to remove air from the system. Under spray pyrolysis conditions nitrogen overpassed continuously through the quartz tube (l= 1.5 m, b= 42 mm) at a flow rate of the 3 l/min. Then atomized droplets of the solution based on Ru and Ti in an ultrasonic generator are further transported by carrier gas to the furnace. After thermal decomposition (or hydrogen reduction) of transported aerosol in furnace the Ru-Ti based nanopowder were collected in a reaction tube and an electrostatic field. XRPD analysis of the nano sized sample powders were 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 $K\alpha_1$ ($\lambda$=1.5406 A) and Cu $K\alpha_2$ ($\lambda$=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 ratio of Ru and $TiO_2$ were tested at 800°C in nitrogen atmosphere in order to analyse a formation of core shell structure.

## Results and Discussion

Products are predicted by thermochemical analysis using Software FactSage under different atmosphere and new mechanism was proposed (Fig. 1.a). New precursor for the synthesis of mixed oxide was developed. The obtained nanopartices were collected in an electrostatic precipitator and analysed by SEM, EDS and XRD analy-

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sis (Fig. 1.b). Spherical nanosized particles of $Ru/TiO_2$ were obtained at 800°C in nitrogen atmosphere. Focused ion beam analysis of obtained particles has shown the formation of core shell structure (Fig. 2). Change of concentration of $Ru/TiO_2$ leads to core-shell structures.

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## References

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**Figures:**

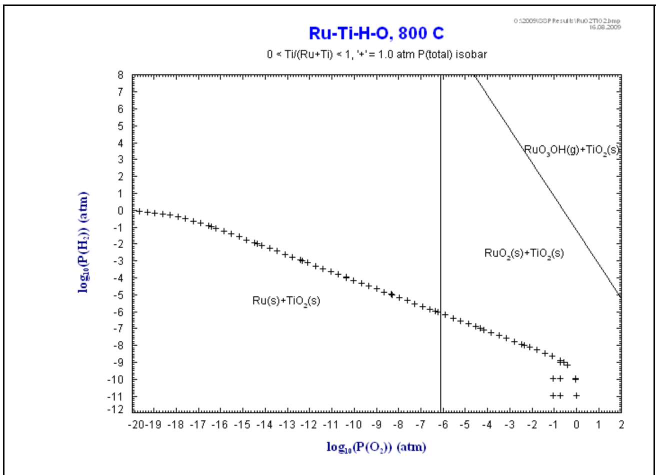


Fig. 1.a: Thermochemical consideration

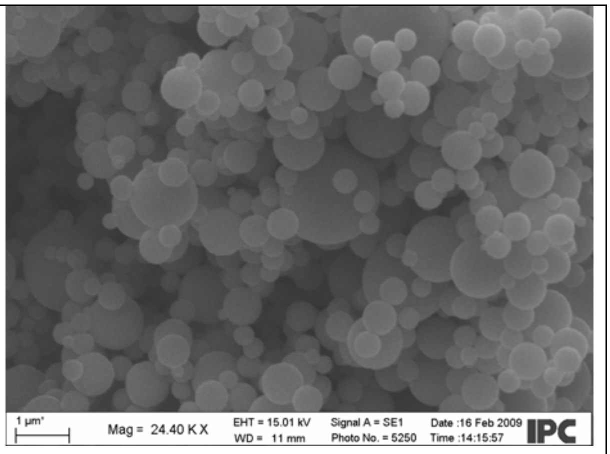


Fig. 1.b: SEM Analysis of $Ru/TiO_2$ Particles

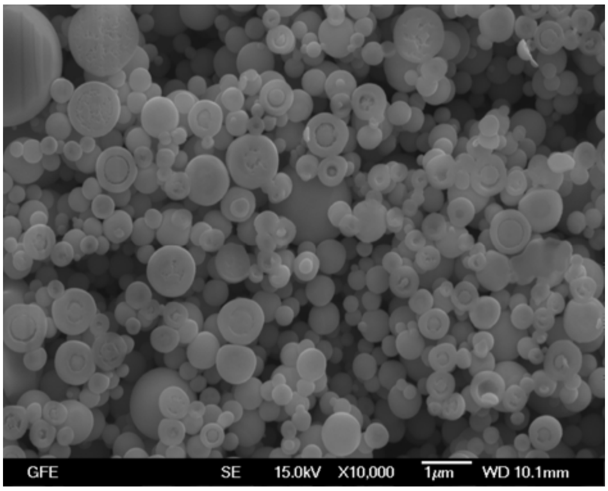


Fig. 2: FIB Analysis of $Ru/TiO_2$ nanoparticles