

Process design of ultrasonic spray pyrolysis synthesis of Ru/TiO₂

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Abstract

The use of ultrasonic spray pyrolysis for the synthesis of nanostructured Ru/TiO₂ 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. XRPD, SEM, FIB, EDS analyses were used in order to analyse morphological characteristic of particles. Formation of core and shell structure was investigated.

Introduction

The target of this study in the frame of DFG-SPP 1423 Program was to develop novel process designs of advanced Ru/TiO₂ nanocatalysts using the ultrasonic spray pyrolysis USP method. Because of a better control of the process and final powder the synthesis of nanostructured Ru/TiO₂ particles from an organic metal salt-solution by USP is a completely new approach contrary to conventional procedures. 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.

Synthesis and characterization of new structure-sensitive materials as Ru/TiO₂ have attracted great attention owing to their promising applications in various technological areas. The preparation of ruthenium- titania based materials to be used as catalysts, chemically durable electrodes and ceramics was described by Balek et al. [1]. RuO₂, crystallizing in a tetragonal rutile structure, has been proposed as the catalyst for several catalytic reactions of technological and environmental importance, for electrodes with high chemical stability toward acids or as the material for very large scale integrated circuits. Moreover, RuO₂ films have been reported to exhibit diffusion barrier properties toward diffusion of oxygen, protecting metallic Ru from oxidation at elevated temperatures. For the Ru/TiO₂ samples with the content of 75 wt% of Ru and 25 wt % TiO₂ the oxidation starts at 300 °C and was stopped at 530 °C before being completed (46.5 % of metallic Ru initially present in the sample was oxidized). It was therefore assumed that a diffusion barrier was formed in the sample, which protected the remaining metallic Ru from further oxidation.

Ru/TiO₂ catalysts were prepared by spray reaction (SPR) and conventional impregnation (IMP) methods by Li et al. [2]. The catalytic activities of SPR fine particles were much higher than those of IMP catalysts for CO₂ hydrogenation. A high temperature reduction greatly promoted the activity of SPR catalyst. A model of surface structure was proposed which exhibits the enhancement of decoration and the formation of more boundaries over Ru/TiO₂. The high activity of SPR catalyst is attributed to the occurrence of new active sites at the metal-support perimeters. EXAFS reveals that the Ru atom was interacting with TiO₂ by oxygen atom so strongly on the SPR catalysts that a part of the Ru atoms, located near the internal interface between Ru particles and TiO₂ support, existed as Ruⁿ⁺ (n<4) cations even if SPR catalyst was subjected to a high temperature reduction.

Core and shell nanoparticles have attracted much attention because a selectivity and improved catalytic activity. Change in the catalytic activity can be affected by core-and shell atoms which can influence the electronic structure. Direct synthesis of Ru-TiO₂ nanoparticles with core and shell structure is not available in literature. Thermal decomposition is one way of depositing the particles forming a shell. Pingali [3] has reported that core-and-shell nanoparticles with Ru as core and Ni as shell were formed in the spray pyrolysis process by varying the constituent ration in the precursor solution. Solid solutions were reported to be prepared by using sol-gel, co-precipitation, solid state reaction, and sonochemical synthesis. In comparison with these methods, aerosol synthesis is scalable. Among aerosol assisted methods, ultrasonic spray pyrolysis method (USP) is often used to prepare fine-grained powders [4].

Particle size, phase purity, and morphology can be easily controlled during the USP process. Huang et al. [5] reported the formation mechanism of these core shell Ti_{1-x}Zr_xO₂ solid spheres is different from that of anatase-

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rutile core-shell-structured titania particles through partial phase transformation mechanism of core shell structure formation during anatase to rutile phase transformation and further decomposition of remaining organic components trapped in the core. Probably the structure of the solid solutions might change via the changes of the concentration of zirconium. Our aim is the synthesis of nanoparticles Ru/TiO₂ in one step by USP method. With regards to that, three subjects were considered: a) Thermochemical modeling of the synthesis b) Influence of molar ratio on phase in nanosized powder, c) formation of core and shell structure

Thermochemical analysis

The following thermochemical analysis was performed at 800 °C.

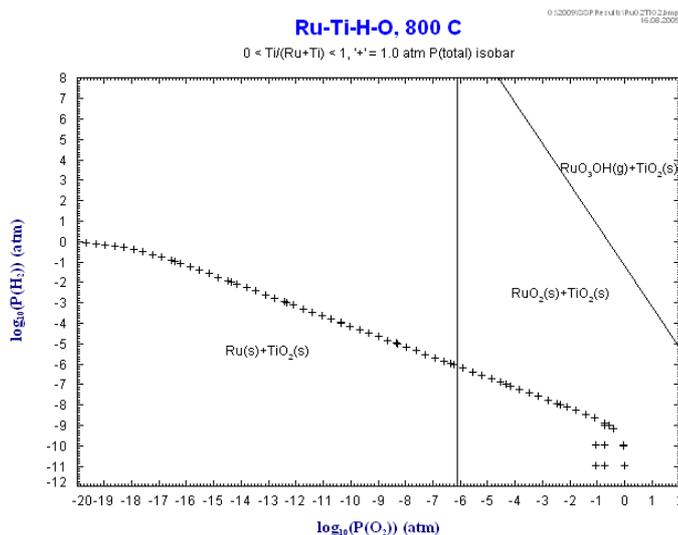


Figure 1. Stability diagram of Ru-Ti-H-O at 800 °C

The formation of solid Ru and TiO₂ has a big probability at 800 °C under an atmospheric pressure. The value of partial pressure of oxygen has a big influence on the formation of our final product based on Ru and TiO₂. Two final products are expected in hydrogen and oxygen atmosphere: RuO₂/TiO₂ and Ru/TiO₂.

Materials and Methods

Tetra-n-butylorthotitanat, ruthenium (III) chloride hydrate and hydrochloric acid were used as precursor for the synthesis of Ru/TiO₂ nanoparticles by ultrasonic spray pyrolysis using the equipment shown schematically in Figure 1. 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.

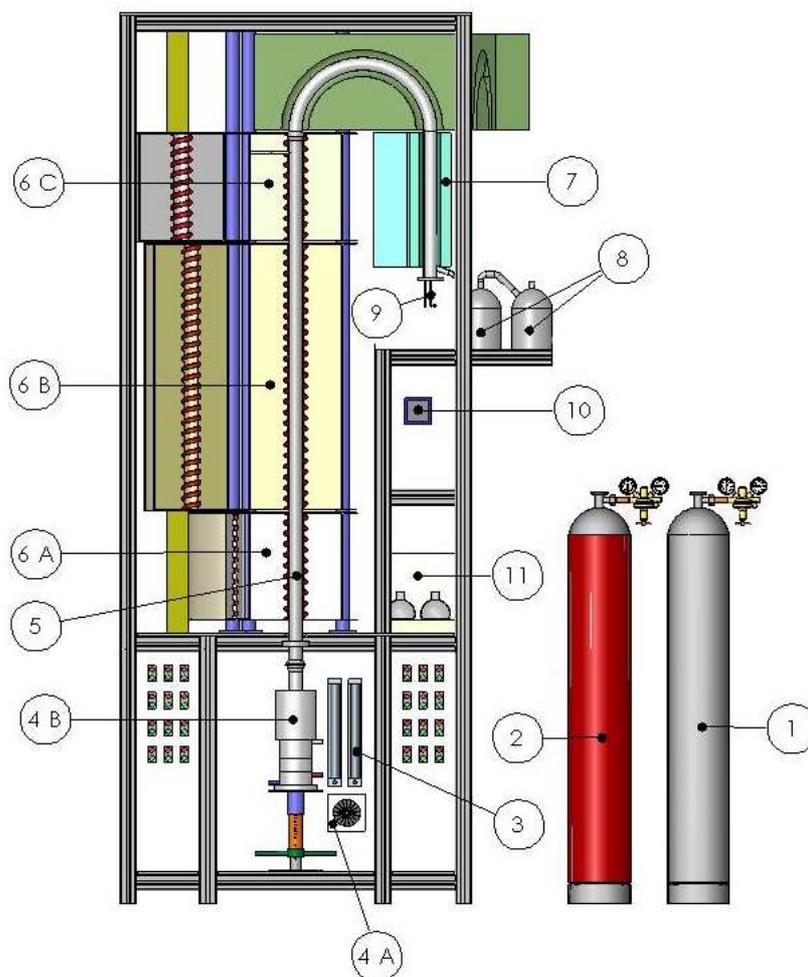


Figure 2. Experimental setup for the USP-synthesis at the IME, Aachen

The most important components: 1. bottle with hydrogen, 2. bottle with nitrogen, 3. flow meter, 4A- electronic unit, 4 B-ultrasonic generator, 5. quartz tube, 6A-furnace (an evaporation zone up to 300 °C), 6 B-furnace (a reaction zone up to 1100 °C), 6 C- a furnace (a heating up to 500 °C), 7.a system for collection of powder, 8. a bottle with water and alcohol, 9. a connection with a high voltage device, 10. a pressure indicator, 11. a vacuum pump.

Nitrogen was flushed from bottle 1 to remove air from the system. Under spray pyrolysis conditions nitrogen (2) overpassed continuously through the quartz tube (5) ($l = 1.5$ 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 (4B) are further transported by carrier gas (2) to the furnace (6). After thermal decomposition of transported aerosol in furnace (6B) the Ru-Ti based nanopowder were collected in a reaction tube and an electrostatic field (7).

Synthesis of nanosized Ru-TiO₂ powder from aqueous solutions of Tetra-n-butylorthotitanat and ruthenium (III) chloride hydrate in a nitrogen atmosphere, flow rate of 3 l/min, with different molar ratios of Ru and Ti: 0.33; 0.22, and 0.17.

An X-ray diffractometer (Bruker D8 Advance) and a scanning electron microscope (ZEISS DSM 982 Gemini) were used for the characterization of the obtained Ru-TiO₂ powders. XRPD analysis of the nanosized sample powders were performed with a Bruker D8 Advance Diffractometer utilizing Bragg-Brentano Geometry and θ - θ 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 α 1 ($\lambda = 1.5406$ Å) and Cu K α 2 ($\lambda = 1.54439$ Å) radiation were recorded, whereas contributions of K- β s are removed from the spectrum. The generator voltage was 40 kV and the current is set to 40 nA. Sample preparation was done by mixing the sample powder with ethanol forming a slurry, subsequently placed on a silicon “zero-background” plate. To minimize additional intensity errors arising from the irradiated sample volume, a variable divergence and antiscatter slit for a sample length of 20 mm was used. Additionally, the instrument was equipped with both primary and secondary soller slits of 2.5°,

and a detector slit of 0.1 mm. The scans were performed in a range of $2\theta = 2-92^\circ$ with a step size of 0.02° and 3 sec. measurement time per step.

XRPD analysis

The experimentally derived diffractograms of the synthesis products with Molar ratios of Ru and Ti: 0.33; 0.22; 0.17 show the overall presence of Anatase, Rutile and Ruthenium. The presence of Ruthenium Oxide, RuO₂, crystallizing isotype to rutile in space group $P4_2/mnm$, was not confirmed, although it might contribute to the background or it probably forms a solid solution with rutile. Quantitative phase analysis and the refinement of structural parameters were performed with the program Topas 4.2 [7] (e.g. Kern and Coelho, 1998; Bruker AXS 2009) applying the Rietveld method [8, 9]. The fundamental parameter approach for apparatusive convolutions was selected for building the start model, and structural models for anatase, rutile and ruthenium were included. The refinement was done on a range $2\theta = 15-92^\circ$ and the background was modelled after Chebychev with a first order polynomial.

The following parameters are included in the refinement (1) sample displacement, (2) 0-error, (3) scale factor, (4) lattice parameters, (5) crystallite size and (6) microstrain. To account for different mass absorption coefficients of the TiO₂ polymorphs (124.5 cm²/g) and ruthenium (176.58 cm²/g), a Brindley correction was applied. The particle radius was set uniformly to 0.5 μm and a packing density of 0.5 was assumed. Finally, relative atom positions for anatase, rutile and the atomic displacement factors for all phases were refined. Ruthenium, crystallizing in the hexagonal space group $P6_3/mmc$, has atoms on the special positions $x = 0.3333$, $y = 0.66667$ and $z = 0.25000$. The unit cell contains 2 formula units. Ruthenium shows a decrease in the crystallite size from 3.29 nm concerning to the precursor solution (Ru/Ti- molar ratio 0.33) to 2.08 nm in the initial precursor solution with Ru/Ti-molar ratio of 0.17. The microstrains are relative large (0.240-0.357) and $\square 0$ is almost uniform for all precursor solutions.

Rutile crystallizes in the tetragonal spacegroup $P4_2/mnm$ and has one refineable oxygen atom in its asymmetric unit, with $x = y$ and $z = 0$. The $x = y$ parameter of natural rutile varies between 0.3045–0.3075, without systematic changes reported. The unit cell contains 2 formula units. The crystallite size of rutile is in the range between 8.90 and 13.2 nm. The microstrain parameter ϵ_0 is not uniform and is between 0.092-0.216.

Anatase, crystallizing in tetragonal space group $I4_1/amd$ has one refineable oxygen atom with $x = y = 0$ and z refineable. For natural heated samples, z -varies between 0.02066-0.02081 nm. The unit cell of anatase contains 4 formula units. The crystallite size of anatase is in a similar order like rutile, and is between 10.7-15.3 nm. The microstrain parameter ϵ_0 values are between 0.17-0.23. The refined z -coordinate of the oxygen atom varies between 0.20722-0.20834. The obtained results of Rietveld analysis are shown at Figs. 3, 4 and 5.

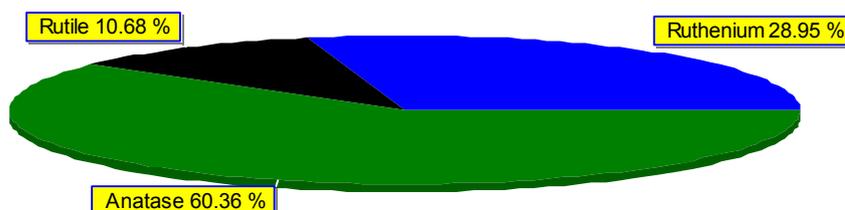


Figure 3. Chemical composition of obtained powder (precursor solution Ru/Ti-molar ratio 0.33)

Decrease of molar ratio of Ru/Ti from 0.33 to 0.22 leads to an increase of rutile- content in an obtained powder.

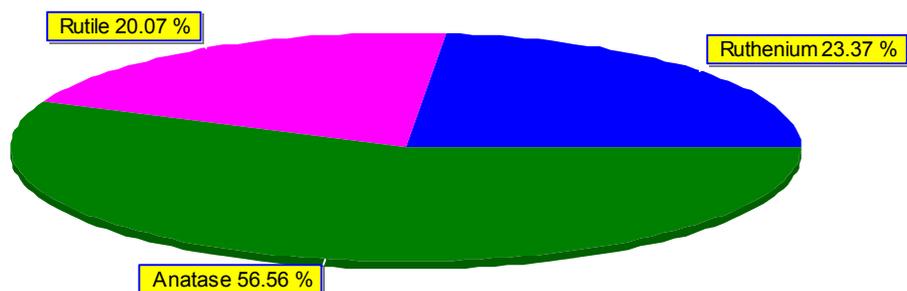


Figure 4. Chemical composition of obtained powder (precursor solution Ru/Ti-molar ratio 0.22)

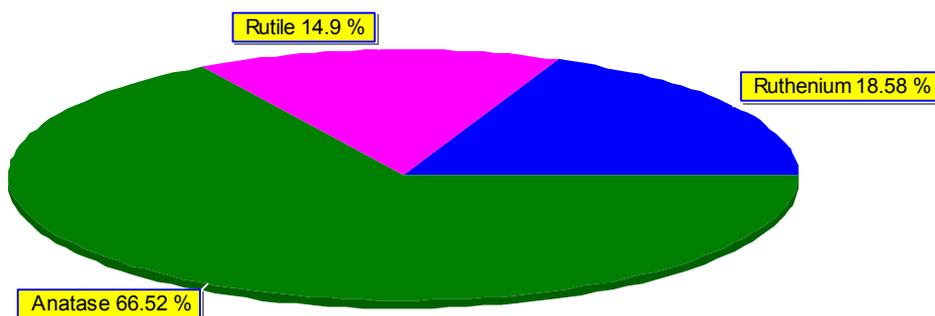


Figure 5. Chemical composition of obtained powder (precursor solution Ru/Ti-molar ratio 0.17)

The proposed mechanism of synthesis:



SEM analysis of obtained powders

Typical analysis of obtained powder was shown at Fig. 6.

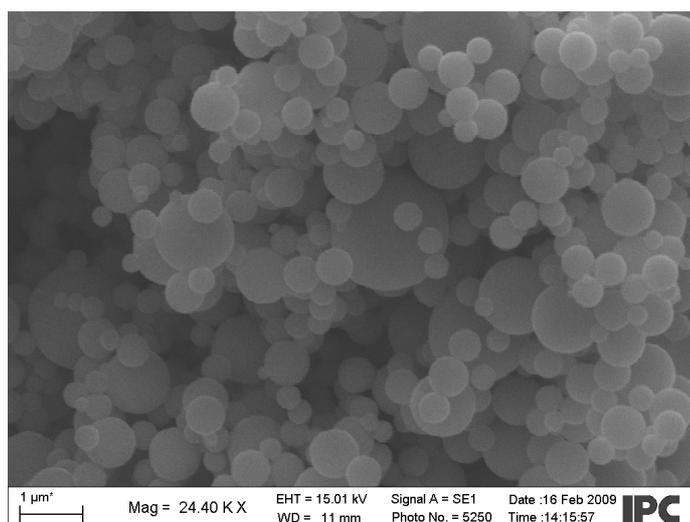


Figure 6. SEM analysis of obtained Ru/TiO₂ powder

The SEM analysis confirms the formation of spherical fine nanosized particles. The following FIB analysis was performed in order to investigate the possible formation of core-and-shell structure. The subsequent SEM

analysis of obtained structure after FIB revealed a core and shell structure. In order to confirm this structure the subsequent Ru/TiO₂ analysis was performed.

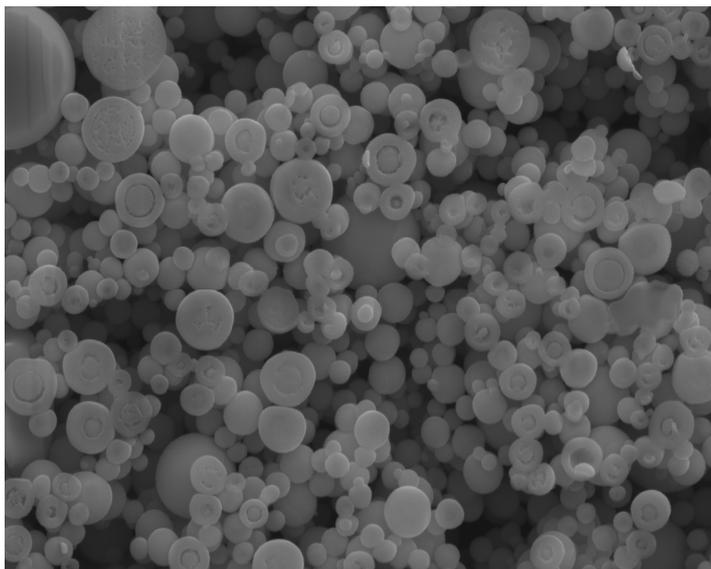


Figure 7. Additional Focused Ion beam FIB analysis of Ru/TiO₂ powder obtained at 800 °C

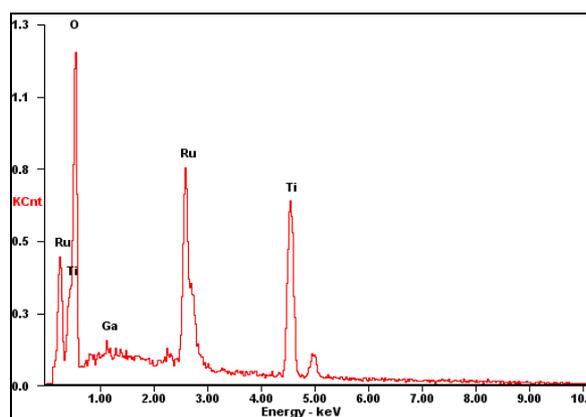


Figure 8. EDS spectra image for the overall nanoparticle shown in Figure 7

The performed EDS analysis has shown that the majority of the core consists of titanium oxide, while the shell is predominately composed of ruthenium. An exact proved mechanism for formation of Ru/TiO₂ nanoparticles with core and shell structure obtained by USP method is not yet present in the literature. According to Pingali [6] the solubilities of components in precursor solution and melting points of Ru and TiO₂ have big importance on the formation of core shell structure. The solubility of Tetra-n-butylorthotitanat (slightly soluble in cold water) is smaller than that of RuCl₃, so TiO₂ precipitates firstly from the solution forming a core. In next step the shell was formed during a RuCl₃ precipitation on the on top of the titanate core. During the thermolysis step, both salts decompose to form Ru and TiO₂, so a Ti/RuO₂ nanoparticles with a core-and shell structure is expected. The nitrogen carrier gas in the reactor seems to be an inert blanket preventing oxidation of ruthenium of the metals during the thermolysis step. According to Vallee [7] the phase relation and melting point are changed when particle size is reduced to the nanometer range (for example: melting point for nanoparticle of gold is decreased about 500 °C). Also the effect of ideally spherically particles might influence on phase relation in Ru/TiO₂ system. Therefore a mechanism of formation Ru/TiO₂ is very difficult to predict and quantitative to prove. Also low temperature in an electrostatic field (about 130 °C) may results in a stronger interaction potential due to low excitation energy.

Conclusion

Ideally spherical nanoparticles of Ru/TiO₂, average diameter between 10 and 800 nm were prepared in a single-step ultrasonic spray pyrolysis process at 800 °C. The experimentally derived diffractograms of the nanosized powder with molar ratios of Ru and Ti: 0.33; 0.22; 0.17 show the overall presence of anatase, rutile

and ruthenium. A core-and shell structure was revealed by FIB and SEM analysis. The performed EDS analysis has shown that the majority of the core consists of titanium oxide, while the shell is predominately composed of ruthenium.

Acknowledgment

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