OPTIMIZATION OF EXTRACTION PROCEDURE USING SUPERCRITICAL AND PRESSURIZED METHANOL AND WATER FOR PREPARATION OF TiO_2-CeO_2 AND ZrO_2 NANOSTRUCTURED POWDERS

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ABSTRACT

The objective of this work was the preparation of TiO_2-CeO_2 and ZrO_2 nanostructured materials in powder form by using pressurized water and supercritical/pressurized methanol and the optimization of this combined extraction procedure in order to yield crystalline polymorphs of these metal oxides. TiO_2-CeO_2 in various molar mixtures and ZrO_2 were synthesized by sol-gel process controlled within reverse micelles of non-ionic surfactant Triton X-114, using titanium (IV) isopropoxide as a titanium precursor. The effect of various extraction conditions (*i.e.* temperature, pressure and extraction solvents volume) on microstructure, textural properties and metal oxides purity was studied by means of nitrogen physisorption, X-ray diffraction, Raman spectroscopy, FTIR spectroscopy and elementary organic analysis. The relationship between the type of processing and properties of synthesized metal oxides was revealed.

INTRODUCTION

Over a long period the nanostructured metal oxides based on TiO_2, CeO_2 and ZrO_2 belong to keenly investigated materials because of their extensive application in sensing films of gas sensors [1,2], as an electrode material in electrochromic devices [3-6], supports of noble metal species in catalysts for VOCs oxidation [7-9] or photocatalysts possessing visible light induced activity [10-15]. The use of supercritical and pressurized fluids introduces an unconventional way of their preparation. It opens up a new scientific challenge concerning the effect of various experimental conditions on the textural, micro/structural, electrochemical, optical and photo/catalytic properties of such-way prepared materials [16-18].

According to our previous research, considering the preparation of metal oxides by a sol-gel process in combination with supercritical/pressurized fluid extractions, the negative features; (i) the relatively high residual carbon content originating from the surfactant(s) used in templated sol-gel syntheses of metal oxides and (ii) the amorphous character of prepared metal oxides after extraction by supercritical carbon dioxide, can be successfully overcome by using pressurized water extraction followed by pressurized/supercritical CH_3OH drying in flow regime [19-21]. Optimizing the experimental conditions of this combined extraction approach should lead to a direct crystallization of metal oxides as well as to a reduction of carbon content that originates from the used chemicals and/or surfactants [20,21].

Thus, the aim of this work was to optimize a combined extraction procedure based on the utilization of pressurized water and supercritical/pressurized methanol in a flow regime in order to yield crystalline polymorphs of TiO_2-CeO_2 and ZrO_2.

MATERIALS AND METHODS

Preparation of TiO_2-CeO_2 and ZrO_2 powders. Cyclohexane (Aldrich, HPLC grade), absolute ethanol (water content max. 0.2 vol.%), non-ionic surfactant Triton X-114 ((1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol, $C_{29}H_{52}O_{8.5}$, Aldrich), zirconium (IV) propoxide solution (70 wt.% in 1-propanol, Aldrich), titanium (IV) isopropoxide (99.999%, Aldrich), cerium (III) nitrate hexahydrate (Aldrich), and distilled water were used as precursors for synthesis. Deionized water (electrical conductivity ~ 0.06–0.08 $\mu S \cdot cm^{-1}$) and methanol (for HPLC) were used as extraction media (solvents) for pressurized extraction and/or supercritical drying.

Titania-ceria (TiO_2-CeO_2) and zirconia (ZrO_2) powders were prepared via sol-gel processing controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane combined with pressurized water extraction and/or supercritical/pressurized methanol drying.

Titania-ceria sols with various Ti:Ce molar ratios (from 97:03 to 70:30) were prepared as follows. In the first step of preparation cerium (III) nitrate hexahydrate was dissolved in absolute ethanol under intense stirring. In the next step cyclohexane was mixed with Triton X-114 and distilled water followed by the addition of ceria sol. The sol was stirred for 20 min. In the final step titanium (IV) isopropoxide was injected into the mixture. The titania-ceria micellar sol was stirred for 20 min. Then the homogeneous transparent sol was poured into Petri's dishes in a thin layer and the dishes were left standing on air for gelation. In general, the titania-ceria sols were prepared keeping the molar ratio of cyclohexane : Triton X-114 : H_2O : $Ti(OCH(CH_3)_2)_4 + Ce(NO_3)_3 \cdot 6H_2O$ at 16.5 : 3 : 3 : 1 and the used amount of absolute ethanol was depending on the amount of dissolved cerium (III) nitrate hexahydrate. The gelation period of individual titania-ceria sols differed quite a lot; it was from 24 hours (for Ti:Ce molar mixtures from 97:03 to 90:10) to 4 days (for Ti:Ce molar mixture 70:30) [22].

In the first step of zirconia sol preparation cyclohexane (38.4 ml) was mixed with Triton X-114 (16.4 ml) and distilled water (0.580 ml) under intense stirring and the mixture was stirred for 20 min. In the next step zirconium (IV) propoxide solution (14.2 ml) was injected into the mixture. This zirconia reverse micellar sol was stirred for next 20 min. Then the homogeneous transparent colourless sol was poured into Petri's dishes in a thin layer (~4 mm) and the dishes were left standing on air for gelation. The gelation period of zirconia sol was ~4 h, however, the zirconia gel was left standing on air for 48 h to leave sufficiently evaporate surface-bonded cyclohexane. In general, the zirconia sol was prepared keeping the molar ratio of cyclohexane : Triton X-114 : H_2O : $Zr(O(CH_2)_2CH_3)_4$ at 11 : 1 : 1 : 1 [20,23].

In the final step of preparation the gels were grinded to small pieces (~2 x 2 mm) and processed/extracted by using pressurized hot water and/or supercritical/pressurized hot methanol in order to produce titania-ceria and zirconia powders.

Extractions were carried out in a home-made extraction unit equipped with the HPLC BETA10 Plus gradient pump (Ecom s.r.o.), the oven operating in the temperature range 25–400 °C, the capillary cooling and the restrictor operating at ambient temperature. For more details about the extraction set-up see Ref. [21]. The gel samples placed in the high-temperature stainless steel cell were extracted/processed in the pressure range 10–30 MPa and the temperature range 150–280 °C, using 0–2 L of deionized water and/or 0–0.55 L of methanol. The flow rate of water and methanol during extraction was kept 3.4–5 mL/min.

Investigation methods. Nitrogen physisorption at 77 K, X-ray diffraction, Raman spectroscopy, FTIR spectroscopy and elementary organic analysis were performed to explore texture, microstructural properties and purity of prepared nanostructured powders.

Nitrogen physisorption measurements at 77 K were performed on the automated volumetric apparatus NOVA2000e (Quantachrome Instruments, USA) or the ASAP 2020 (Micromeritics, USA) after degassing of powders at 25 °C for 24 h under 1 Pa vacuum.

XRD patterns were measured by the PANalytical MPD difractometer in the conventional focusing Bragg-Brentano geometry, with variable slits, using Ni-filtered CuKα characteristic radiation. The PIXcel PSD detector was used to collect the scattered intensity in the diffraction angle range 10º–120º. From the XRD analysis the phase composition and the size of crystallites (coherently scattering domains) were determined similarly in Ref. [24]. The measured XRD data were simulated using the whole powder pattern modelling [25] software MStruct [26], which is an extension of the FOX [27] program. The crystallites were assumed spherical with a log-normal distribution of diameters [24,25,28]. The NIST LaB_6 line profile standard was measured in the same experimental arrangement to characterize instrumental effects.

Raman spectra were collected on a Smart System XploRA^{TM} (Horiba Jobin Yvon, France) using 532 nm laser source. An Olympus microscope BX 41/51 with an objective magnification of 50 was used to focus the laser beam on the sample placed on an X–Y motorized sample stage. Filter was used to reduce laser beam to 1% of initial intensity and grating 1200 gr./mm was used. Raman spectra were taken from five different places within each sample.

Fourier-transform infrared (FTIR) spectra were recorded in the range of 500 – 4000 cm^{-1}. Samples were measured by ATR technique with diamond crystal on Nicolet 6700 FT-IR (Thermo Scientific, USA).

The purity (elementary carbon in wt.%) of materials was specified on the Vario EL III apparatus from Elementar. Approximately 5 mg of solid material was burned in oxygen atmosphere at temperature up to 1200°C. Gaseous products (N_2, CO_2, H_2O and SO_2) were purified, separated to individual components and analyzed on TCD detector. Analyses were triplicated. The detection limit of the apparatus was 0.1 abs.%.

RESULTS

TiO_2-CeO_2. Based on our previous study about the crystallization of TiO_2 [21] the effect of extraction by pressurized water and pressurized methanol at 200°C and 10 MPa on crystallization of TiO_2 doped with various Ce molar amounts (3-30 mol.%) was investigated. Figure 1 reveals that under these extraction conditions all titania-ceria molar mixtures crystallized only to titania crystalline phases – anatase and brookite – and with increasing Ce amount in TiO_2 the crystallization of brookite was suppressed, resulting for 30 mol.%Ce/TiO_2 in crystallization to pure TiO_2 anatase (Figure 2). This observation was quite surprising and interesting in comparison with a thermally treated 30 mol.%Ce/TiO_2 sample at 500°C and 800°C (Figure 2) [22]. It can be seen that even at 500°C the 30 mol.%Ce/TiO_2 sample was amorphous and at 800°C it crystallized to the brannerite-type cerium titanate phase, $CeTi_2O_6$. At elevated extraction temperature 250°C at 10 MPa the 30 mol.%Ce/TiO_2 sample crystallized to the mixture of TiO_2 anatase and CeO_2 cubic which was evidenced in XRD pattern by (111), (200) and (311) *hkl* reflections at 28.5, 33.1 and 56.3°.

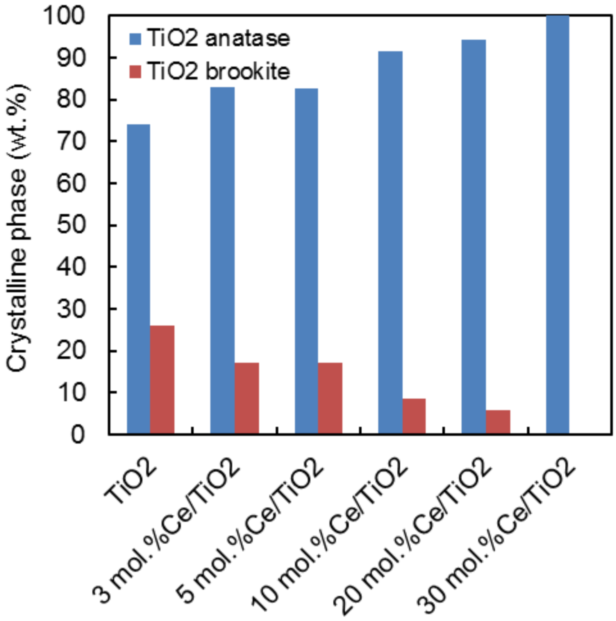

Figure 1: Phase composition of individual crystalline phases for TiO_2 doped with various Ce molar amounts after processing by pressurized water and pressurized methanol at 200°C and 10 MPa.

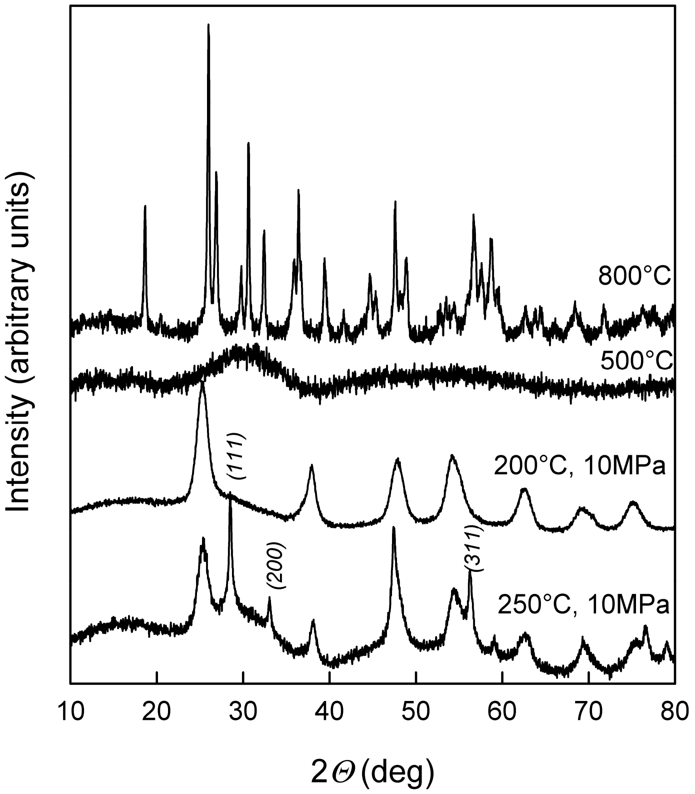

Figure 2: XRD patterns of TiO_2 doped with 30 mol.% of Ce, processed by conventional thermal treatment at elevated temperature (500°C and 800°C) and by using pressurized water and pressurized/supercritical methanol (at 200°C or 250°C and 10 MPa).

ZrO_2. Extraction temperature played also a key role in crystallization of zirconia. Moreover, increased pressure promoted the crystallization. At 10 MPa zirconia was amorphous up to 200°C and it crystallized to a mixture of tetragonal and monoclinic phases from ~235°C. At 30 MPa the crystallization of zirconia took place already at 200°C. The effect of temperature at 10 MPa and 30 MPa during extraction by water and methanol on a specific surface area of ZrO_2 can be seen in Figure 3. A steep decrease of specific surface area can be attributed to the formation of ZrO_2 nanocrystallites.

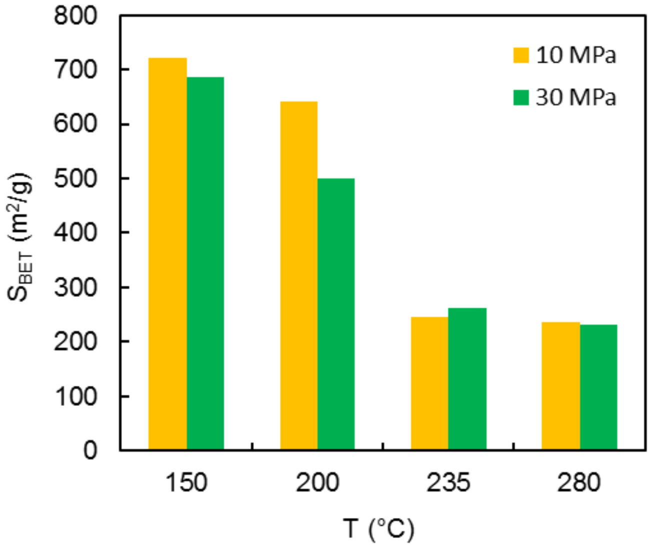

Figure 3: Effect of temperature at 10 MPa and 30 MPa during processing by water and methanol on a specific surface area of ZrO_2.

CONCLUSION

The extraction procedure based on the utilization of pressurized water and pressurized/supercritical methanol was investigated for preparation of crystalline polymorphs of TiO_2-CeO_2 and ZrO_2. It was proved that pressurized water causes crystallization of metal oxides and pressurized/supercritical methanol is responsible for the improvement of their purity (*i.e.* for the elimination of organic phase originating from the used surfactant). The crystallization of TiO_2-CeO_2 as well as ZrO_2 to a mixture of TiO_2 anatase and CeO_2 cubic or ZrO_2 tetragonal and monoclinic phases was achieved, but the extraction conditions are very specific for individual metal oxides and their molar mixtures and must be optimized. The decrease of specific surface area of synthesized metal oxides can be associated with the crystallites formation.

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