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Reverse micelles directed synthesis of TiO_2–CeO_2 mixed oxides and investigation of their crystal structure and morphology

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ABSTRACT

The synthesis of TiO_2–CeO_2 mixed oxides based on the sol–gel process controlled within reverse micelles of non-ionic surfactant Triton X-114 in cyclohexane is reported. The crystallization, phase composition, trends in nanoparticles growth and porous structure properties are studied as a function of Ti:Ce molar composition and annealing temperature by in-situ X-ray diffraction, Raman spectroscopy and physisorption. The brannerite-type $CeTi_2O_6$ crystallizes as a single crystalline phase at Ti:Ce molar composition of 70:30 and in the mixture with cubic CeO_2 and anatase TiO_2 for composition 50:50. At Ti:Ce molar ratios 90:10 and 30:70 the mixtures of TiO_2 anatase, rutile and cubic CeO_2 appear. In these mixtures TiO_2 rutile is formed at higher temperatures than conventionally. Additionally, the amount of a present amorphous phase in individual mixtures was estimated from diffraction data. The porous structure morphology depends both on molar composition and annealing temperature. This is correlated with the presence of carbon impurities of different character.

1. Introduction

In the past years titania–ceria mixed oxides have been intensively examined due to their high application potential as sensing film gas sensors [1,2], an electrode material in electrochromic devices [3–6], coatings for self-cleaning surfaces [7], photocatalysts with activity induced under visible light ($\lambda > 410$ nm) [8–13] and support of catalysts [14,15]. Various preparation methods based on the precipitation [14] or the more promising sol–gel process [1–3,6,7,9–11,15–20] have been suggested and studied. The syntheses have been realized using either titanium alkoxide or titanium chloride together with cerium salts (i.e. cerium chloride or cerium nitrate) as metal precursors. However, titanium alkoxides as well as titanium chlorides are highly reactive in hydrolytic conditions (even at ambient humidity) and during the sol–gel synthesis the precipitation or the flocculation can occur as a consequence of fast hydrolysis. Therefore, chelating agents and surfactants in a role of templates are used to prevent this behaviour and to control the hydrolytic-polycondensation reaction during the sol–gel synthesis [9,15,19–21]. As a result of such syntheses a homogeneous transparent sol can be obtained, which can be applied not only for preparation of powders, but also transparent nanoparticulate thin films. Moreover, it was found out that preparation conditions (i.e. the Ti:Ce molar composition, the annealing temperature and the atmosphere character) significantly affect structural properties and the crystallization of individual titania–ceria mixtures [1,9,13,18,20,22–25]. The formation of cerium titanates have been observed in the specific range of Ti:Ce molar ratios [18,22]. Besides that, the thermal treatment in a reducing atmosphere gives cerium titanate phases with Ce^{3+} such as the reddish-brown Ce_2TiO_5 and $Ce_2Ti_2O_7$ and the chestnut $Ce_4Ti_9O_{24}$, while the thermal treatment in air produces cerium titanates with Ce^{4+} such as the yellow $CeTi_2O_6$ and $CeTiO_4$ [3,13,18,20,22–25].

This paper reports on the synthesis of nanoparticulate TiO_2–CeO_2 mixed oxides based on the sol–gel process controlled within reverse micelles of non-ionic surfactant Triton X-114 in cyclohexane for the first time. Besides the presentation of new preparation approach of titania–ceria mixed oxides, this work focusses on the study of the effect of various Ti:Ce molar compositions and the annealing temperature on the crystallization, the phase composition and the crystallite-growth of formed nanocrystalline phases, since according to the literature data mentioned above the preparation route plays the key role. A quantitative X-ray diffraction (XRD) phase analysis including an estimation of amorphous phase content was done. Raman spectroscopy was used as a complementary method to in-situ XRD to reveal the crystallization phenomenons which are not recognizable by XRD. The porous structure morphology of titania–ceria mixtures annealed in a broad range of temperatures (350–900 °C)

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was studied by nitrogen physisorption. Unusual features in properties of porous structure in a specific range of annealing temperatures were revealed and were nicely correlated with different character of identified impurities.

2. Material and methods

2.1. Preparation

Cyclohexane (Aldrich, HPLC grade), nonionic surfactant Triton X-114 ((1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol, $C_{29}H_{52}O_{8.5}$, Aldrich), absolute ethanol (water content max. 0.2 vol.%), titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, 99.999%, Aldrich), cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Aldrich) and distilled water were used as precursors for the synthesis.

Titania–ceria mixed oxides powders with various Ti:Ce molar ratios (90:10, 70:30, 50:50 and 30:70, expressed in mol.%) were prepared via sol–gel processing controlled within reverse micelles of nonionic surfactant Triton X-114 in cyclohexane. The samples are marked using following notation: Tix–Cey, where x and y are the molar percents of Ti and Ce, respectively. In the first step of preparation the ceria sol was prepared: cerium (III) nitrate hexahydrate (0.3994 g) was dissolved in absolute ethanol (3 ml) under intense stirring. In the next step cyclohexane (16.4 ml) was mixed with Triton X-114 (14.4 ml) and distilled water (0.4 ml) followed by the addition of ceria sol. The sol was stirred for 20 min. In the final step titanium (IV) isopropoxide (2.43 ml) was fluently injected into the mixture. The precursor micellar titania–ceria sol (with Ti:Ce = 90:10) 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 up to the conversion of the sol into the gel. In general, the precursor 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 3–5 ml, 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 h to one week (for Ti:Ce molar mixtures from 90:10 to 50:50) to ~4 weeks (for Ti:Ce molar mixture 30:70) and it showed a strong dependence on ambient temperature and humidity. The gels were thermally treated in air at 350 °C for 4 h with the heating rate 1 °C/min in order to produce as-prepared Tix–Cey differently yellow-coloured powders.

2.2. Methods

XRD patterns were measured by the PANalytical-MPD diffractometer in the conventional focussing Bragg–Brentano geometry with variable slits using Ni-filtered Cu$K\alpha$ characteristic radiation. PIXcel PSD detector was used to collect the scattered intensity in the diffraction angle range 10°–120°. The sample was placed in a MRI high-temperature chamber in a ceramic holder. The heating (up to 900 °C) was performed with a radiant heater placed around the sample. During in-situ XRD experiments the as-prepared powders were annealed in 50 °C step between 350 and 900 °C in air for 45 min and the XRD patterns were recorded. From the XRD analysis the phase composition and the size of crystallites (coherently scattering domains) were determined. The measured XRD data were simulated using the whole powder pattern modelling [26] software MStruct [27], which is an extension of the FOX [28] software. The crystallites were assumed spherical with a log-normal distribution of diameters [26,29,30].

For X-ray fluorescence, nitrogen physisorption and Raman spectroscopy studies the set of conventionally thermally treated samples for each Tix–Cey mixture was prepared in the temperature range 350–900 °C (grain size < 0.160 mm). Each powder was prepared by calcination of the gel sample at 350 °C for 4 h with the heating rate 1 °C/min (corresponding to 'as-prepared sample') followed by annealing at required temperature for 45 min with the heating rate 1 °C/min. Exact ex-situ reproduction of the in-situ XRD heating was too much technically ambitious.

X-ray fluorescence analysis was performed on the ARL 9400 XP sequential WD-XRF spectrometer. The spectrometer was equipped with Rh anode end-window X-ray tube type 4GN fitted with 75 μm Be window. All peak intensity data were collected under vacuum conditions using the software WinXRF. The generator settings-collimator-crystal-detector combinations were optimized for all 79 measured elements with analysis time of 6 s per element. The obtained data were evaluated by standardless software Uniquant 4. The analyzed powders were pressed into pellets about 5 mm thick and the diameter of 40 mm without any binding agent and covered with 4 μm supporting polypropylene film.

Nitrogen physisorption measurements were carried on the automated volumetric apparatus ASAP 2020 Micromeritics after drying of powders at 105 °C for 12 h under 1 Pa vacuum. The nitrogen adsorption–desorption isotherms were measured at −196 °C. The specific surface area was calculated according to the classical Brunauer–Emmett–Teller (BET) theory for the p/p_0 range = 0.05–0.25 [31]. The mesopore surface area and the micropore volume were determined by the t-plot method [32]. The pore–size distribution (pore radius 10^0–10^2 nm) was calculated from the adsorption branch of the adsorption–desorption isotherm by the Barrett–Joyner–Halenda (BJH) method [33] via the Roberts algorithm [34] and with the assumption of the cylindrical pore geometry. The Lecloux–Pirard standard isotherm [35] was employed for the t-plot as well as for the pore-size distribution evaluation.

Raman spectra were collected using a dispersive Nicolet Almega XR spectrometer equipped with the Olympus BX 51 microscope. Excitation laser source (473 nm) with an incident power of 5 mW with 512 expositions with 0.5 s duration was used for collecting the spectra. The laser beam was focussed to a spot of 0.6 μm in diameter. The incident energy was minimized to avoid thermal effects as a consequence of the laser irradiation. Spectral resolution of the instrument was 1.93 cm^{-1} and the spectrometer was calibrated using crystalline silicon standard with line at 520 cm^{-1}. The band widths at half maximum (FWHM) were determined by spectral deconvolution after normalizing the spectral band.

3. Results and discussion

3.1. Phase analysis based on in-situ XRD and Raman spectroscopy

Via reverse micelles controlled sol–gel processing titania–ceria powders in various Ti:Ce molar ratios were synthesized; Ti90–Ce10, Ti70–Ce30, Ti50–Ce50 and Ti30–Ce70. The crystallization of individual molar mixtures was studied over as-prepared samples from 350 °C up to 900 °C using in-situ XRD measurements. Raman spectroscopy over 'ex-situ' annealed samples was used as a complementary method to XRD, allowing to reveal the crystallization phenomenons which are not recognizable by XRD. The selected XRD patterns of all synthesized titania–ceria mixtures are shown in Fig. 1a–d and Fig. 2. The phase compositions of individual Ti–Ce mixtures depending on the annealing temperature evaluated from XRD data are depicted in Fig. 3a–d. Raman spectra of titania–ceria mixtures are depicted in Fig. 4a–d. The volume weighted crystallite-sizes and the trends in