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CHARACTERIZATION OF HYDROTHERMALY SYNTHESIZED ZIRCONIA NANOPOWDERS

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ABSTRACT

In this paper, a hydrothermal method for synthesis of zirconia nanopowders: pure and with incorporated Si⁴⁺ ions is presented. Zirconyl chloride and tetraethyl orthosilicate were used as precursors. As prepared powders were annealed at 600 °C and their structural (XRD), morphological (TEM) and textural (BET method) properties were obtained. It has been shown that by using hydrothermal synthesis method pure monoclinic ZrO₂ highly crystalline powder can be obtained with crystallites of about 25 nm. Incorporation of Si⁴⁺ ions induced stabilization of tetragonal crystalline phase at room temperature, decreasing particle sizes to about 3-6 nm and increasing specific surface area of nanopowders.

INTRODUCTION

Zirconia (ZrO₂) is an important and widely used ceramic material. In recent years, much attention has been paid to the preparation of high surface area nano-zirconia due to its wide application as a catalyst and catalyst support, sorbent, oxygen sensor, etc.[1]. The objective of this publication was to synthesize zirconia nanopowders with high specific surface area without surfactants/additives. High surface area, small particle sizes, is correlated with crystalline phase of zirconia: monoclinic phase demands large volumes for development ($D \geq 25$ nm), metastable tetragonal phase is common for small particles ($D \leq 20$ nm). We choose hydrothermal method for synthesis because it can be easily controlled and reproduced, it can be carried out at moderate temperatures and it already has been used to prepare nanosized powders. In order to influence specific surface area and crystallinity of zirconia we introduced Si⁴⁺ ions in zirconia matrix during synthesis.

EXPERIMENTAL

The following commercial reagents were used: Zirconyl chloride octahydrate (reagent grade, SigmaAldrich, 98%), TEOS (Tetraethyl orthosilicate, Aldrich, 98%), Sodium hydroxide (Aldrich, $\geq 97\%$). All chemicals were used as received. In all experiments deionized water from Mili Q system was used. Pure and Si^{4+} incorporated zirconia nanopowders were synthesized by hydrothermal treatment. In a Teflon vessel (125 ml volume) 50 ml of 2 M NaOH, 2 g of zirconyl chloride powder for pure ZrO_2 , and appropriate amount of TEOS for powders with Si^{4+} ions (2.3 mM or 23 mM, samples ZrO_2 -1 and ZrO_2 -2, respectively) were added. Dispersion was vigorously stirred for 1 h and then autoclaved for 24 h at 150 °C. After that, the powder was separated from the washing solution by centrifugation. The XRD powder patterns were obtained using a Philips PW 1050 powder diffractometer with Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology and sizes of photocatalysts were obtained using transmission electron microscopy, TEM, JEOL JEM 1400, accelerating voltage 120 kV. Textural properties of our samples were determined using nitrogen adsorption/desorption parameters. The nitrogen adsorption was performed at -196 °C and relative pressure interval between 0.05 and 0.98 in automatic adsorption apparatus (Sorpomatic 1990 Thermo Finningen).

RESULTS AND DISCUSSION

Typical XRD patterns of pure ZrO_2 powder and ZrO_2 powders with incorporated Si ions are shown in Fig. 1.(a and b). The pure ZrO_2 powder has peaks that can be indexed as monoclinic- ZrO_2 (Baddeleyite JCPDS 65-1025) (Fig. 1.(a)). Monoclinic ZrO_2 is the stable phase formed at temperatures less than 1170 °C in the absence of additives (where it transforms to tetragonal and then to cubic phase at temperatures above 2370 °C up to the melting point at 2680 °C) [2,3]. ZrO_2 nanopowders with incorporated Si ions are much less crystalline with broad peaks, Fig. 1.(b), which can be assigned to tetragonal crystalline structure (JCPDS 81-1544). ZrO_2 -1 crystallized partially in monoclinic phase moving the most intensive peak of tetragonal crystalline phase to lower 2θ value (from 30.2° to $\sim 29.5^\circ$). Powder with higher concentration of Si ions showed a mixture of t- ZrO_2 and amorphous SiO_2 ; the low intensity broad peak at approximately $2\theta = 22^\circ$ corresponds to amorphous SiO_2 . Particle sizes were calculated using Debye-Scherrer equation. Pure ZrO_2 had diameters of about 25 nm and both samples with incorporated Si ions had diameters of about 3 nm. As reported previously, the monoclinic phase is the stable phase at low temperatures, but the tetragonal phase is the first formed in nucleation

process and heat treatment [4]. The presence of the metastable tetragonal phase at low temperatures can be attributed to several factors such as chemical effects (the presence of anionic impurities), structural similarities between the tetragonal phase and the amorphous zirconia phase that is precursor of crystallization, as well as particle size effects (based on the lower surface energy in the tetragonal phase compared to the monoclinic phase).

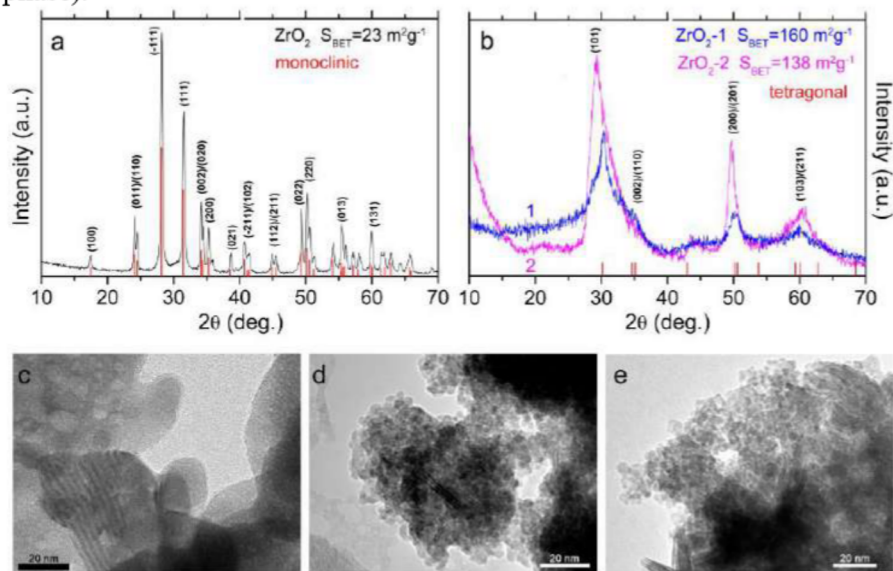


Figure 1. XRD patterns and specific surfaces of (a) pure ZrO_2 and (b) ZrO_2 with incorporated Si^{4+} ions. Typical TEM images of ZrO_2 based photocatalysts: (c) pure and (d, e) with incorporated Si^{4+} ions.

In Fig. 1.(c,d,e) a typical TEM images of pure zirconia (c) and zirconia powders with incorporated Si ions (d and e) are presented. Pure ZrO_2 is constituted of large particles, $D \geq 20$ nm and even larger agglomerates of about 100 nm, although this size should be taken cautiously as it was difficult to distinguish boundaries between entities. These findings are in agreement with diameter/sizes of crystallites calculated from XRD. Crystalline domains gained using Debye-Scherrer equation can be smaller than real sizes of the particles due to presence of amorphous phase present as well. In addition to well defined crystalline nanoparticles, with visible crystal planes, some defects can also be observed like spots with diameters of 5–10 nm. These spots are small amorphous zones embedded in the crystalline zirconia matrix [4]. In Fig. 1. (d and e) small particles of 3–6 nm can be seen in both samples with Si ions, ZrO_2 -1 and ZrO_2 -2, with sizes in

agreement to those calculated using Bebye-Scherrer equation. Also some larger elongated particles/agglomerates ($D \approx 20$ nm) with defect/twinned structure can be observed. In these larger particles with twinned domains, most probably started the $t \rightarrow m$ transformation [5], but the volume fraction of monoclinic crystalline phase still being too low in order to be registered by XRD. It can be seen that Si incorporation process through hydrothermal synthesis process and subsequent annealing, suppresses effectively the growth of nanoparticles. Textural properties of ZrO_2 nanopowders were investigated using BET method. Obtained specific surface areas of the samples are indicated in Fig. 1. (a and b). As can be seen, incorporation of Si^{4+} ions in zirconia induced a significant increase of specific surface area - S_{BET} of powders with Si ions was 7 times larger than pure zirconia. The specific surface area is slightly larger when smaller concentration of Si ions (15 mol%) was incorporated in zirconia matrix, as a consequence of saturation of particle surface with Si ions or presence of amorphous silica layer on the surface of the particles for sample ZrO_2 -2.

CONCLUSION

The hydrothermal method was successfully used for synthesis of pure zirconia and zirconia with incorporated Si^{4+} ions. Pure ZrO_2 had monoclinic crystalline phase and particles of about 25 nm, powders with incorporated Si ions remained in metastable tetragonal crystalline phase with diameters of about 3–6 nm. Significant increase of specific surface area was achieved by incorporation of Si ions in zirconia matrix, which was one of the main goals that we wanted to achieve with this study.

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