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Hydrothermal preparation of porous materials from a rutile–quartz concentrate

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Abstract

Synthesis of porous TiO_2 from a Yarega rutile–quartz concentrate by using a simple low cost hydrothermal method is reported. Samples were characterized by the X-ray diffraction (XRD) method, energy-dispersive X-ray spectroscopy (EDX), inductively coupled plasma optical emission spectroscopy (ICP-OES) and Brunauer–Emmett–Teller (BET) analysis to determine the specific surface area. The as-synthesized porous material contains 96.95 wt% TiO_2 with rutile structure and is characterized by high surface area -5.0–5.5 m^2/g. Formation of porous materials may result from the dissolution of impurities from the rutile matrix of the starting rutile–quartz concentrate during the hydrothermal process.

Keywords: A. Hydrothermal; B. Porous materials; D. Titanium dioxide

1. Introduction

Titanium dioxide is one of the most important and widely used compounds owing to its several unique physical and chemical properties [1–4]. These properties make it attractive for various technological applications, including catalysis [5], production of hydrogen [6], conversion of light-to-electric energy in solar cells [7], etc. Applications of TiO_2 are strongly related to the surface area and local microstructure. Therefore, porous as well as nanostructured TiO_2 with a large surface area and specific morphology has attracted great attention [8,9]. Till now, many methods, such as anodization [10], template techniques [11], hydrothermal processes [12], and vapor depositions [13] were used to synthesize porous TiO_2. However, technique complexity and expensive reagents limit its industrial application.

In the last few years it has finally been demonstrated that titanium minerals can be directly used in the preparation of TiO_2 nanostructures and porous materials [14–21]. Combination method, consisting of ball milling, carbothermic reduction and hydrochloric acid leaching, was proposed for the preparation of nanosized synthetic rutile from natural ilmenite [14]. Synthesis of rutile TiO_2 nanorods from ilmenite through the simple two-step procedure of ball milling and acid treatment was demonstrated [15]. TiO_2 nanotubes from natural leucoxene [16,17], and nanowires from ilmenite [18] by the hydrothermal method were obtained. Formation of mesoporous TiO_2 from ballmilled ilmenite in aqueous solutions of sulfuric acid was reported [19]. These techniques allow producing high-demanded titania products directly from high-grade mineral feedstock. Nevertheless high quality titania preparation from low-grade mineral feedstock is an important industrial problem.

Yarega oil titanium deposit in Komi Republic, Russia is one of the largest titania deposits all over the world. Yarega deposit contains a low-grade rutile mineral with a great amount of quartz impurities [22]. Rutile–quartz concentrate is a product of oil titanium ore benefication by using the method of flotation with following kerasine extraction of heavy-oil. Therefore, the Yarega rutile–quartz concentrate cannot be used as a feedstock for the titanium industry due to expensive mineral processing.

Synthesis of porous TiO_2 from a Yarega rutile–quartz concentrate by using a simple low cost hydrothermal method

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is reported. The phase composition, morphology, surface area and formation mechanism of these porous materials are discussed.

2. Experimental

2.1. Synthesis

The rutile–quartz concetrate from the Yarega oil titanium deposit, the Republic of Komi, Russia was used as a starting material. Rutile–quartz concentrate was provided from OJSC (YaregaRuda). The size of the particles was in the range of 200–400 μm. 25 g of the rutile–quartz concetrate and 5 M of NaOH aqueous solution were placed inside the stainless steel autoclave (miniclave drive, BuchiGlassUster). The mixture was heated and stirred at 200 °C and 1.6 MPa for 1 h. At the end of the hydrothermal reaction, it was cooled down to room temperature and filtered. The precipitate was washed with a 0.5 M HCl solution and distilled water. Washed samples were dried in the oven at 90 °C for 2 h.

2.2. Characterization

Chemical compositions of the rutile–quartz concetrate and as-synthesized sample were determined by inductively coupled plasma optical emission spectrophotometer (ICP-OES) (Thermo Fischer Scientific, iCAP DUO 6300 ICP). Structural characterization was performed using the Riqaku D/MAX 2500 X-ray diffractometer equipped with CuKα radiation ($k=1.5418$ Å).

SEM images and elemental mapping of the particles were observed with the scanning electron microscopy (SEM, JEOL, JSM-6610LV). Samples elements were identified by the energy-dispersive X-ray spectroscopy (EDS). Specific surface area was measured by the N_2 adsorption/desorption method with the Quantachrome Nova1000e volumetric instrument at liquid nitrogen temperature (77 K). Samples were degassed at 150 °C overnight prior to the measurement. BET surface areas were calculated by the multipoint method using adsorption data in the relative pressure (P/P_0) with a range of 0.05–0.3.

3. Results and discussion

Chemical compositions of the rutile–quartz concetrate and as-synthesized samples are shown in Table 1. The rutile–quartz concetrate contains 63.19 wt% TiO_2, 31.04 wt% SiO_2, 3.22 wt% Al_2O_3 and 1.05 wt% of other impurities. The as-synthesized samples contain 96.95 wt% TiO_2. During the hydrothermal process, the quantities of impurities decreased. The sum of impurities is not above 3.05%. The quantities of SiO_2 and Al_2O_3 decreased to 0.93 wt% and 0.71 wt% respectively. It is well known, that SiO_2 and Al_2O_3 can be leached in sodium hydroxide solutions. So, the SiO_2 removing efficiency reaches almost 97%.

Fig. 1 shows the XRD patterns of the rutile–quartz concetrate and as-synthesized sample. The rutile–quartz concetrate consists of a mixture of rutile phase of TiO_2 and SiO_2. The diffraction peaks of other impurities, such as Al_2O_3 and Fe_2O_3 of the starting rutile–quartz concetrate, are not observed. Most of those impurities may exist as a part of a solid solution. As shown in Fig. 1, the impurity phases are not detected in the as-synthesized sample by XRD. The XRD patterns of the as-synthesized sample indicate that all the peaks were matched with the standard XRD pattern of rutile phase of TiO_2. The peaks are very narrow, indicating high crystallinity. Nearly all impurity phases entered into the liquid phase, while TiO_2 was still in the solid phase. As shown in Fig. 1, hydrothermal treatment of the rutile–quartz concetrate produce the high crystallinity rutile phase of TiO_2.

Table 1
Chemical composition of the rutile–quartz concetrate and as-synthesized samples (wt%).

Oxide	Rutile–quartz concetrate	As-synthesized samples
TiO_2	63.19	96.95
SiO_2	31.04	0.93
Al_2O_3	3.22	0.71
Fe_2O_3	1.50	1.05
K_2O	0.57	0.01
MgO	0.15	0.09
Nb_2O_5	0.09	0.12
P_2O_5	0.09	0
Na_2O	0.07	0
V_2O_5	0.05	0.05
ZrO_2	0.01	0.03
CaO	0.01	0.06

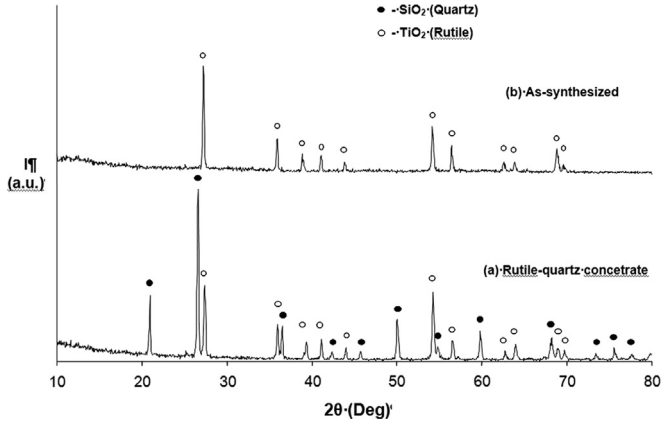

Fig. 1. XRD patterns of the starting rutile–quartz concetrate and the as-synthesized sample.

Fig. 2 shows a SEM image of the starting rutile–quartz concetrate, which consists of large particles with a typical size of 200–400 μm. During the hydrothermal process, the size of the particles changed slightly (Fig. 3). However particles of the prepared sample possess a porous morphology. The BET specific surface area of the as-synthesized porous materials is approximately 5.0–5.5 m^2/g, while that of the starting rutile–quartz concetrate is as low as 0.1–0.2 m^2/g. An increase in the BET specific surface area is a result of the formation of porous TiO_2 particles during the hydrothermal process (Fig. 3).

A more detailed higher magnification image of the starting rutile–quartz concetrate surface is presented in Fig. 4. From the