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Ceramics International 31 (2005) 555–557

CERAMICS INTERNATIONAL

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Synthesis of nanocrystalline rutile

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Received 22 May 2004; received in revised form 18 June 2004; accepted 22 July 2004
Available online 16 September 2004

Abstract

Nanocrystalline titanium dioxide (TiO_2) in the rutile phase has been obtained by homogeneous precipitation using urea and $TiOCl_2$. A mixture of urea and $TiOCl_2$ is heated on a hot water bath at 65–75 °C to precipitate rutile powders. X-ray diffraction (XRD) studies on these oven-dried powders indicated the formation of single-phase rutile. Raman scattering experiments were also performed to confirm the formation of the rutile phase.

Transmission electron microscopy (TEM) investigations revealed the average particle size of these powders to be 40 nm.

Keywords: A. Powders; Chemical preparation; B. X-ray methods; B. Electron microscopy; D. TiO_2

1. Introduction

Titanium dioxide (TiO_2) is an important industrial material as a main component of paint, pigment, cosmetics and as a support for vanadium $DeNO_x$ catalyst. It has also been used for optical coatings, beam splitters and anti-reflection coatings because of its high dielectric constant and refractive index. There are reports on its use as a humidity sensor and high temperature oxygen sensor [1–4]. The three crystalline polymorphs of TiO_2 are anatase, rutile and brookite. Rutile is a thermodynamically stable phase possessing a smaller band gap energy (3.0 eV) than the anatase phase (3.2 eV). A large number of preparation methods of TiO_2 have been investigated and reported in the literature [1–4]. The starting materials have a profound influence on the formation of TiO_2 nanocrystallites with well-defined crystalline morphology. Nanocrystalline anatase is generally synthesized as hydrothermal methods and sol–gel methods using titanium alkoxides. Recently, we have reported the preparation of ultrafine TiO_2 powders by the citrate gel and digestion method [1,2]. In the present work, a homogeneous precipitation method using urea is employed to produce ultrafine rutile powders. Urea is used as a fuel, precipitating agent and as a resin former with formaldehyde. When urea is used along with nitrate salt of a cation and heated at 400 °C, the exothermic reaction between nitrate (oxidant reactant) and urea (fuel) leads to formation of corresponding nanocrystalline oxides. The main advantage is that necessary heat for synthesis is obtained directly from the reaction [5,6]. In the case of homogeneous precipitation, urea acts as a precipitant. Since urea decomposed around 100 ° C to produce carbon dioxide and ammonia thereby increasing the pH of the solution at which metal cation precipitation takes place [7]. In yet another method [8] urea forms polymeric resin with formaldehyde along with reactants and on the decomposition of the resin at higher temperatures, the final product is formed. To the best of our knowledge, this method has not been reported in the literature for the preparation of rutile TiO_2 powders.

2. Experimental

All the reagents used in the present work are of AR grade. $TiCl_4$ was diluted with ice-cold distilled water to

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0272-8842/$30.00
doi:10.1016/j.ceramint.2004.07.003

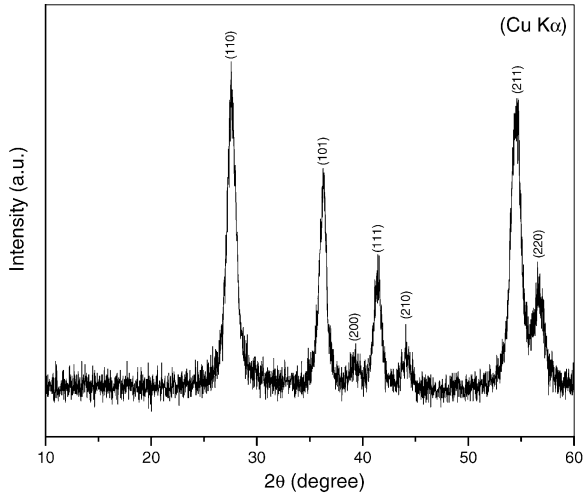

Fig. 1. XRD of rutile powders obtained after drying the precipitate 100 °C.

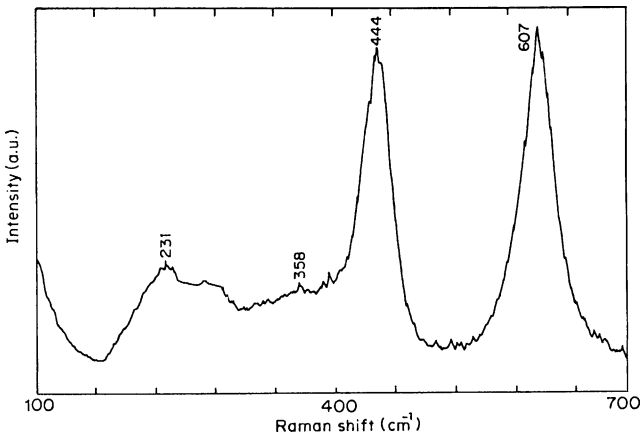

Fig. 2. Raman shift in rutile powders.

form $TiOCl_2$ solution (0.2 M). To this solution a known quantity of urea was dissolved and this mixture was heated on a hot water bath. The ratio of Ti to urea was 1:5. Then the crystalline powder precipitated was filtered and oven dried overnight. Techniques such as XRD (Philips PW 1710 Diffractometer) and BET surface area measurements (Nova 1200 Instrument) were employed to characterize these powders. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 10–80 ° for the period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was used to determine the lattice parameters. The TEM picture was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid. Raman scattering experiments were performed in the region 100–700 cm^{-1} in the back scattering mode using SPEX 1403 reflection grating type double spectrometer to confirm the TiO_2 rutile phase.

3. Results and discussion

Fig. 1 shows the XRD for the oven-dried samples at 100 °C. During heating on water bath, urea decomposes into CO and NH_3. The observed d-lines match the reported values for the rutile phase. Samples prepared under identical conditions [3] without urea showed mixed phases of anatase and rutile (not shown). The calculated lattice parameters for

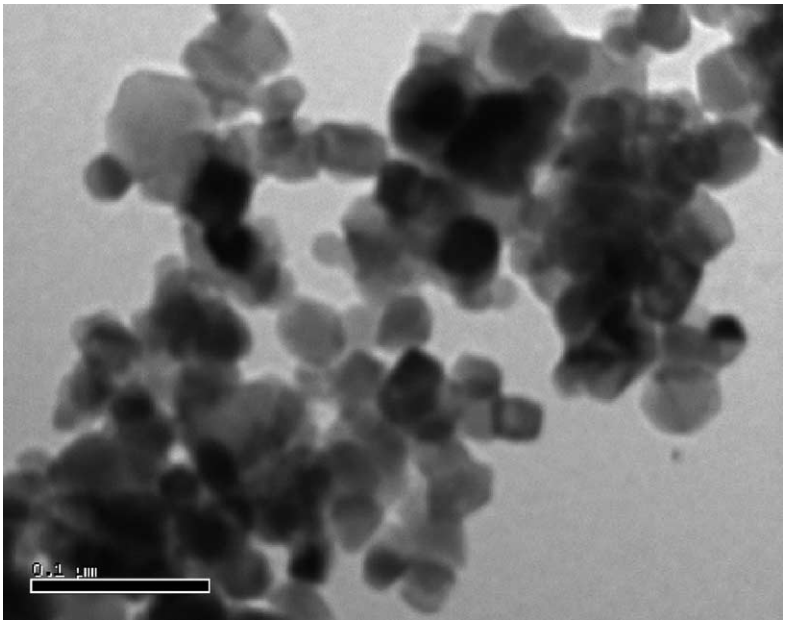

Fig. 3. TEM pictures of rutile powders.

rutile are $a = 4.564$ Å and $c = 2.945$ Å. The surface area of these powders was found to be 100 m^2/g. Fig. 2 shows the Raman spectrum of TiO_2 powders in rutile phase. The band near 608 cm^{-1} was identified as A_{1g} mode, the band near 446 cm^{-1} as the E_g mode for the rutile phase [4]. The small differences in assigning peak wavenumbers from the literature are considered to be arising from intragrain defects present in the sample. The Raman bands for rutile are similar to that reported in the literature [4]. The average particle size of rutile phase is found to be 40 nm and the particles of rutile phase are observed to be agglomerated (Fig. 3). The crystallite size measurements were also calculated using the Scherrer equation, $D = k\lambda/\beta \cos\theta$ where D is the crystallite size, k is a constant (=0.9 assuming that the particles are spherical), λ is the wavelength of the X-ray radiation, β is the line width (obtained after correction for the instrumental broadening) and θ is the angle of diffraction. The average particle size obtained for rutile phase from XRD data is 50 nm.

It is well known that both anatase and rutile TiO_2 can grow from TiO_6 octahedra and that the phase transition proceeds by the rearrangement of the octahedra. Arrangement of octahedral through face sharing initiates the anatase phase while the edge sharing leads to the rutile phase. In aqueous medium, protonated surfaces of TiO_6 octahedra easily combine with –OH groups of other TiO_6 octahedra to form Ti–O–Ti oxygen bridge bonds by elimination water molecule. The protonation followed by the possible face-sharing TiO_6 octahedra will result in formation of anatase phase while edge sharing leads to rutile phase. In the present case, edge sharing is favoured leading to rutile phase. The fine powders of rutile phase obtained by this method are possibly potential candidates for air and water purification photocatalysts.

4. Conclusions

Rutile TiO_2 is obtained by homogeneous precipitation method using $TiOCl_2$ and urea. TEM investigations show that their average particle size to be 40 nm.

Acknowledgment

The authors are thankful to Department of Science and Technology, Grant No: SP/S1/H-19/2000, New Delhi, India for financial support.

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