Microwave-assisted synthesis of bismuth oxide

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Abstract

Single phase and ultrafine bismuth oxide was synthesized via microwave-assisted hydrothermal synthesis. The effect of reaction parameters (temperature/pressure and pH) on the product phase composition and morphology was discussed. The transformation of bismuth hydroxide into bismuth oxide was controlled by pH value and it was accelerated by time and temperature. The phase composition of reaction products was strongly dependent on pH value. The amorphous products were obtained at acidic pH conditions and the crystalline single phase product α-Bi_2O_3 phase was obtained at pH ≥12. The particle size was reduced from micrometric to nanometric size in the presence of a chelating agent. The bismuth hydroxides into bismuth oxides transformation mechanism, consisting in polycondensation of Bi – OH bounds to Bi – O – Bi bridges and crystallization of Bi_2O_3, was proposed.

Keywords: microwave-assisted synthesis, bismuth oxide, nanocrystalline

I. Introduction

Bismuth oxide and binary or ternary systems based on bismuth oxide are often used as catalytic materials for partial oxidation of hydrocarbons, such as propene, isobutene or methane [1], and for photocatalytic applications [2,3]. The low particle size or high specific surface area and also the good chemical and phase purity are the most important properties of bismuth oxide. Bismuth oxide exists in five polymerphic modifications. The low temperature α and high temperature δ phases are stable, whereas β, γ and ω are metastable at high temperatures [4–6]. Crystalline bismuth oxide was prepared by conventional high temperature solid state reaction of bismuth salts [7] or by means of mechanochemical synthesis [8, 9]. Non-conventional methods such as hydrothermal synthesis [10] and sonochemical synthesis [3] were also used for bismuth oxide preparation. However most of the methods are however based on precipitation reactions of bismuth salts and calcination of bismuth products [5,6,12–15]. Nucleation and growth of particles in the course of hydrolysis / condensation of bismuth salts can be controlled by means of additives such as polyethylenglycol [5], polyvinylpyrollidon [3], urea [14] and / or citric acid [13]. However, no information is available about bismuth oxide synthesis in the microwave field. The study of direct synthesis of bismuth oxide by hydrolysis and condensation of bismuth nitrate in microwave field is the main goal of this paper.

II. Experimental Procedure

Preparation of samples

Two different routes of bismuth oxide preparation were studied. The first one consists of two steps. In the first step, the bismuth hydroxide was prepared by precipitation reaction of bismuth nitrate with ammonium hydroxide solution (1 M). The precipitated bismuth hydroxide was separated and washed with water to neutral pH. In the second step, the pH of bismuth hydroxides was adjusted to a value in the range of 6–12 by nitric acid and / or ammonium hydroxide. Suspensions were placed in microwave field and transformed under hydrothermal conditions at temperatures from 100 to 220°C. The microwave reactor (Multiwave 3000, Anton Paar, Austria) working at a frequency of 2.45 GHz and a maximum power of 1400 W was used for experiments.

In the second synthesis way the influence of the chelating agent (polyethyleneglycol) on product precipitation was investigated. Aqueous solutions of reactants

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prepared by dissolving bismuth nitrate (2.0 M), sodium hydroxide (4.0 M) and polyethyleneglycol (PEG 4000 – 0.05 M) were cooled to a temperature below 100°C and then mixed in molar ratio 0.12 / 0.44 / 0.002, respectively. The suspensions created immediately after the mixing of reactants were placed in the microwave reactor and treated at temperatures from 40 to 60°C, with or without stirring during treatment. All the products were separated by centrifugation, washed with water to neutral pH and dried at 110°C. All chemicals used in the experiments were of AR grade and bought from Sigma Aldrich.

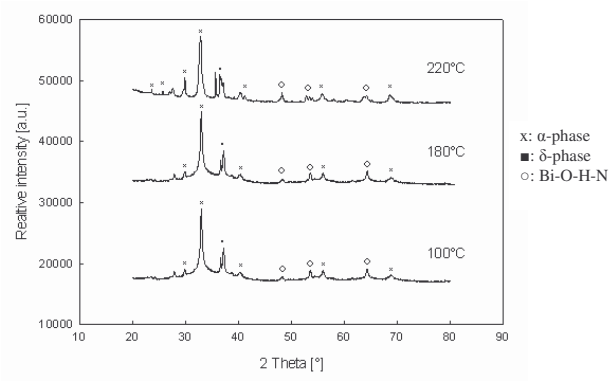


Figure 1. The effect of reaction temperature on the phase composition of products synthesized 1h at 100°C, 180°C, 220°C, pH = 7 (x α-phase, ▪ δ-phase, ○ Bi-O-H-N)

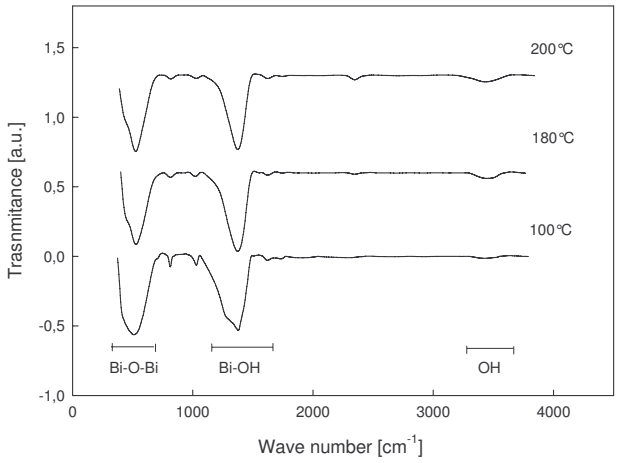


Figure 2. IR spectrum showing the amount of OH groups contained in the product synthesized at pH = 7 and different temperature (100°C, 180°C, 220°C)

Characterization of powders

The phase composition was determined by X-Ray diffraction analysis, K_{Co} wavelength (X´pert, Philips, Netherlands). The morphology of powder products was studied by scanning microscopy (SEM XL 30, Philips, Netherlands). The specific surface area (SSA_{BET}) was determined by the BET method (Chembet, Quantachrome, USA). For the estimation of the OH group content in $Bi_X(OH)_Y(O)_Z$ infrared spectroscopy (Nicolet, Thermo Corporation, USA) and thermal analysis Pyris 1 (Perkin Elmer, USA) were used.

III. Results and Discussion

Synthesis of bismuth oxide by precipitation reaction in MW field

The phase composition of reaction products prepared at pH = 7 at different reaction temperatures is given in Fig. 1. The crystalline products prepared at temperatures of 100°C, 180°C and 220°C containing two bismuth oxide phases (α–Bi_2O_3 and δ–Bi_2O_3) and also an unknown phase were found in the XRD spectra. From IR spectra given in Fig. 2 it follows that the unknown phase is probably bismuth hydroxo-oxide $Bi_X(OH)_Y(O)_Z$, which can be transformed into single-phase Bi_2O_3 by calcination at 600°C. Water bound as OH groups was released in the course of calcination as observed by two peaks (Fig. 3) at 505°C and 560°C probably because of different positions of OH groups in the bismuth hydroxide-oxide structure. The main influence on the composition of reaction products was that of the pH of reaction medium. Amorphous $Bi_X(OH)_Y(O)_Z$ products (Fig. 4) containing large amounts

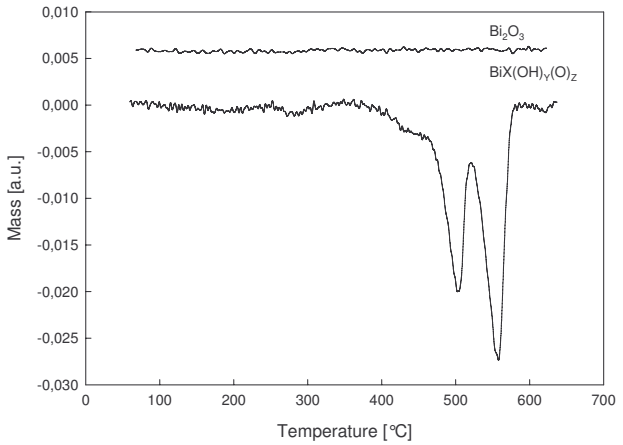


Figure 3. Differential thermal analysis of $Bi_X(OH)_Y(O)_Z$ and α-Bi_2O_3

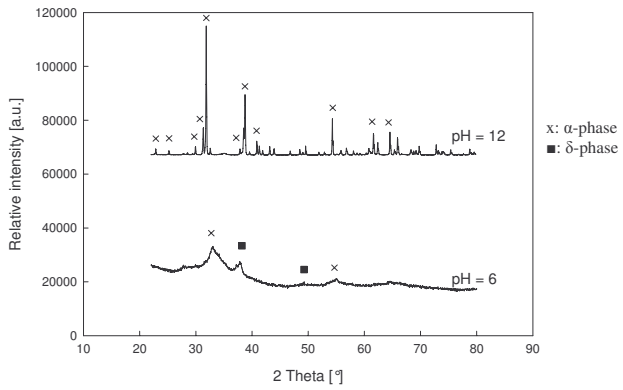


Figure 4. The effect of pH on the phase composition of as-synthesized Bi_2O_3 at pH = 6–12, 100°C, 2h) (x α-phase, ▪ δ-phase)

of OH groups (Fig. 5) with high specific surface area (SSA_{BET} = 39.0 m²/g) were created under slightly acidic conditions – pH = 6. The morphology of the product prepared at 100ºC is given in Fig. 6a. The particles were of flaky shape with a maximum particle size of 5 μm. Under basic conditions (at pH ≥ 12) single-phase α-Bi_2O_3 products with small specific surface areas (SSA_{BET} =0.2 m²/g) were created. IR spectra given in Fig. 5 showed no OH groups in the product. The morphology of product particles prepared at 100°C under the basic conditions (Fig. 6b) is similar to morphology of the particles prepared under acidic conditions (Fig. 6a). The effect of pH on the composition of reaction products is given in the Table 1.

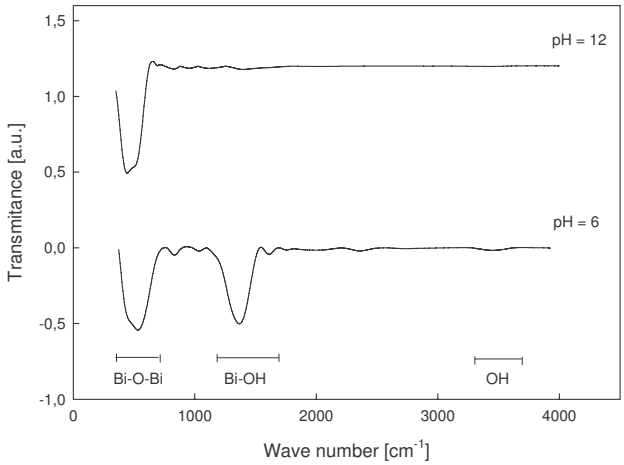


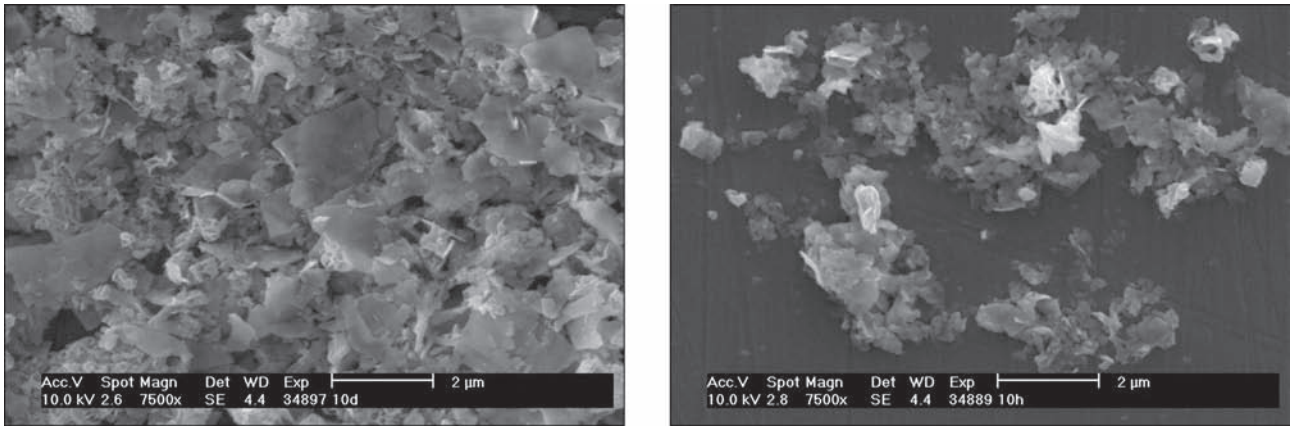
Figure 5. IR spectrum showing the amount of OH groups contained in the product synthesized at 100°C and at different pH (6, 12)

Synthesis of bismuth oxide in the presence of chelating agent and MW field

Nanometric particles of bismuth oxide prepared by precipitation of bismuth nitrate under the basic conditions and in the presence of polyethyleneglycol at 90 °C/2h were published by Li [5]. The results given in this paper concern a similar synthesis but carried out in the stirred microwave reactor at lower temperatures (40°C and 60°C) and shorter time (30 min). XRD spectra of the products are given in Fig. 7. The crystalline products containing mainly α-Bi_2O_3 and traces of δ–Bi_2O_3 were prepared in both cases (40°C and 60°C). The needle-like particles of α-Bi_2O_3 (Fig. 8) had the specific surface area in the range of 0.2–0.6 m²/g. In comparison with the results of Li [5] the nanometric spherical particles were not obtained. However, the synthesis carried out in the microwave field without stirring the reaction mixture lead to α-Bi_2O_3 nanoparticles with a small amount of OH groups (Fig. 9). The needle-shaped particles with high specific surface area (SSA_{BET}=21.6 m²/g) are given in Fig. 10.

Reaction mechanism of Bi_2O_3 formation

On the basis of the above results a possible reaction mechanisms is described bellow. Reaction of Bi^{3+} salt started by hydration and was followed by hydrolysis. Bismuth hydroxide is created in this first phase of reaction mechanism. In the second phase of reaction mechanism the condensation of OH groups proceeds and is accompanied by the formation of bismuth oxide species. In particular this second step is strongly dependent on the pH of reaction medium. The formation of bis-



a) b)

Figure 6. SEM pictures showing the particle shape and size of product synthesized at 100°C, 2h: a) pH = 6 and b) pH = 12

Table 1 The effect of pH on the reaction product prepared at pH = 6 – 8 – 10 – 12, 100°C, 2h

pH	6	8	10	12
Reaction product	$Bi_x(OH)_yO_z$	$Bi_x(OH)_yO_z$	$Bi_x(OH)_yO_z$	α-Bi_2O_3
SSA_{BET} [m²/g]	34.5	37.9	39.9	0.2

muth oxide species is catalyzed by OH anions and proceeds through the formation of oxo-ligands, which are stable at pH ≥ 12.

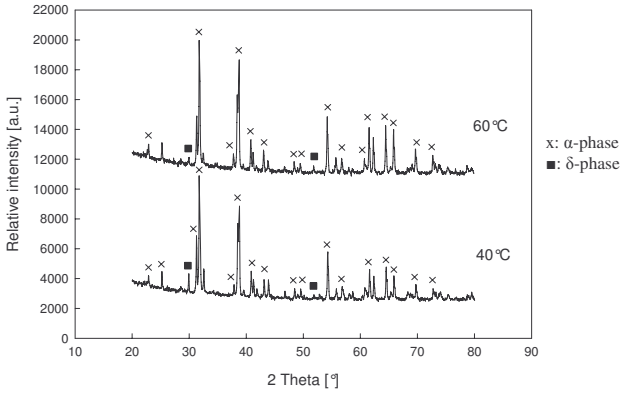


Figure 7. The effect of reaction temperatures (40°C, 60°C) on the phase composition of products synthesized with the addition of chelating agent (the reaction parameters: pH = 12, 30 min) (x α-phase, ▪ δ-phase).

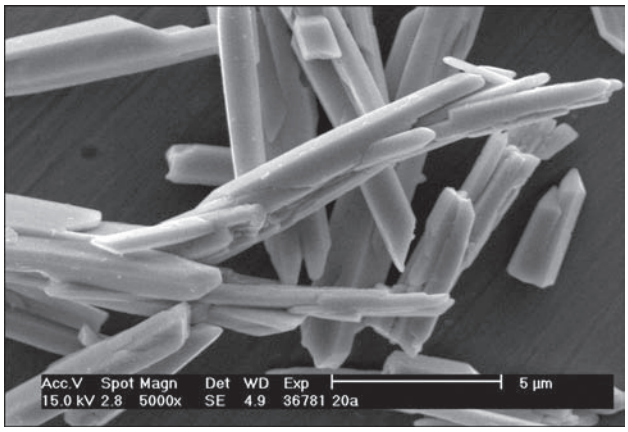


Figure 8. SEM picture showing the particle shape and size of product synthesized with chelating agent and with stirring during the procedure (40°C / 30 min / pH = 12)

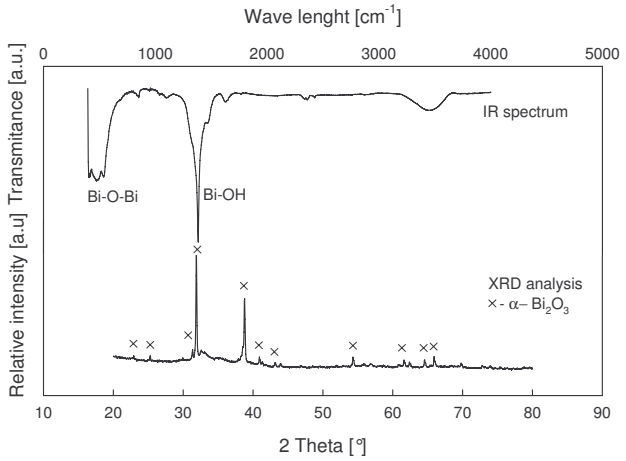


Figure 9. XRD spectrum of product synthesized at 40°C / 30 min / pH = 12 without stirring, and IR spectrum of the same product

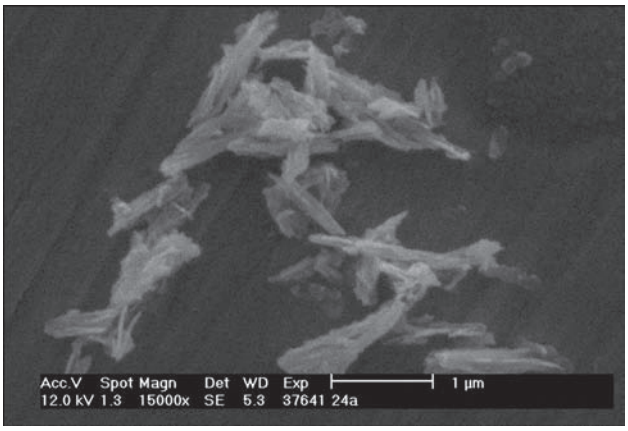


Figure 10. SEM picture showing the particle shape and size of product synthesized with chelating agent and without stirring during the procedure (40°C / 30 min / pH = 12)

Microwave field accelerated the processes of hydrolysis and condensation under basic conditions and therefore α-Bi_2O_3 was formed at temperatures and times substantially lower than α-Bi_2O_3 synthesized without using microwave irradiation [5,13]. The acceleration of reaction process is the cause of non-conventional heating of the whole volume of reaction mixture by microwave field.

IV. Conclusions

The nanocrystalline bismuth oxide with SSA_{BET} = 21.4 m^2/g was successfully prepared via microwave-assisted synthesis by precipitation from bismuth nitrate solutions with admixture of chelating agent to control the reaction rate and the final properties of powder product (such as particle size, morphology and phase composition). The time of preparation and reaction temperature was reduced using microwave-assisted synthesis.

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