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Obtaining tin (II) oxide by a chemical method

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Tin (II) oxide formation has been carried out by reacting tin powder with nitric acid at various concentrations (4 M; 4.5 M; 5 M) in a glass beaker under spontaneous stirring at various heating temperatures (100°C; 90°C; 80°C). The resulting sample in the form of a yellowish precipitate was cooled, washed using distilled water and acetone, dried in a mortar and filtered. The samples were iodometrically tested and characterized using differential thermal analysis (DTA), optical microscopy (OM) for morphology and phase analysis (XRD). The results of the iodometric test showed different oxidations. At the 4 M concentration with all heating temperature variations, Sn^{2+} oxidation was observed. According to the results of OM study, the surface morphology was irregular and there was a residue of tin that did not completely react with nitric acid. The results of the thermal test (DTA) showed that the sample experienced thermal decomposition at temperatures of 419°C and 426°C. XRD results indicate that the formation of SnO_2 has occurred.

Keywords: tin (II) oxide, SnO_2, precipitate, morphology.

Утворення оксиду олова (II) хімічним методом. *Perdinan Sinuhaji, Wahyu Bambang Widayatno, Agus Sukarto Wismogroho, Cherly Firdharini, Paulina Aryati Samosir*

Отримано оксид олова (II) шляхом взаємодії порошку олова з азотною кислотою з різними концентраціями (4 М; 4,5 М; 5 М) при різних температурах нагріву (100°C; 90°C; 80°C). Зразки протестовано на йодометрію, проведено диференційно-термічний аналіз (DTA), вивчено морфологію зразків (оптична мікроскопія, ОМ), зроблено рентгенівський аналіз сформованої фази (XRD). Результати йодометричного тесту показали різне окислення. Концентрація 4 М при всіх варіаціях температури нагріву приводила до окислення Sn^{2+}. Морфологія поверхні нерівномірна, присутній залишок олова, який у повному обсязі прореагував з азотною кислотою. Результати випробування теплових властивостей (DTA) показали, що зразок термічно розкладається при температурах 419°C і 426°C. За результатами XRD-тесту відбулося утворення SnO_2.

Получен оксид олова (II) путем взаимодействия порошка олова с азотной кислотой с различными концентрациями (4 М; 4,5 М; 5 М) при различных температурах нагрева (100°C; 90°C; 80°C). Образцы протестированы на йодометрию, проведен дифференциально-термический анализ (DTA), изучена морфология образцов (оптическая микроскопия, ОМ), проведен рентгеновский анализ сформированной фазы (XRD). Результаты йодометрического теста показали различное окисление. Концентрация 4 М при всех вариациях температуры нагрева приводила к окислению Sn^{2+}. Морфология поверхности была неравномерной и присутствовал остаток олова, который не полностью прореагировал с азотной кислотой. Результаты испытания термических свойств (DTA) показали, что образец термически разлагается при температурах 419°C и 426°C. Результаты XRD-теста показывают, что произошло образование SnO_2.

1. Introduction

Metal tin can form compounds that can be used as a catalyst, for example tin (II) Oxide (SnO) [1]. Tin (II) oxide (SnO) is a *p*-type semiconductor which has metastable chemical properties at room temperature; at high temperatures, it transforms to Sn_2O_3 which directly forms SnO_2 [2–4]. Tin (II) oxide is unstable at all temperatures and easily forms SnO_2 [5]. At a temperature of 300°C to 550°C, SnO directly converts into tin and SnO_2 [6]; at a temperature of 500°C, in a closed volume, SnO, SnO_2, tin are not formed, but β-tin oxide is formed [7]; at temperatures in the range of 400°C–1040°C, SnO is decomposes into tri-tin tetraoxide which then becomes SnO_2 [8]. SnO is stable at temperatures of 300°C–600°C [9]. In recent times, SnO has been patented as a useful material for lithium ion rechargeable batteries. This is due to the very high theoretical capacity (875 mA·h/g) [10–12] compared to graphite (372 mA·h/g) and SnO_2 (783 mA·h/g) [13]. SnO can be formed in several methods. The methods used in the manufacture of SnO are the homogeneous precipitation method [14], the gas phase condensation method [15], the condensation/evaporation laser method in the diffusion chamber [16], the hydrothermal method [17] and the solvothermal method [18]. Also SnO can be formed chemically by using chemical spray pyrolysis method [19] and sonochemical method [20]. SnO can be used to speed up the decomposition process. SnO has a large surface-to-volume ratio, so it can be used as a photocatalyst. SnO and other tin oxids can be used in a wide variety of scientific and technological applications [21] as coatings [22], catalysts [23, 24], chemical gases, for thermal reflection and in microelectronics [25].

The purpose of this work is to analyze the efficiency of formation of tin (II) oxide by a direct chemical reaction using nitric acid as an oxidizing agent.

2. Experimental

This study was carried out in two stages: first, the dilution of nitric acid, and then the reaction process between tin powder and nitric acid. The raw materials used are tin powder and nitric acid. The instrumentation used in this research: electric stove, magnetic stirrer, glass beaker, dropper, volumetric flask, vacuum pump, filter paper, Erlenmeyer pumpkin, Sartorius BSA 2245-CW analytical scale, spatula. The methods used: differential thermal analysis (DTA), X-ray diffraction (XRD), and optical microscopy (OM).

2.1 Nitric acid dilution process

65 % nitric acid was converted to molar units; then the dilution method was used to calculate 4 M, 4.5 M and 5 M. After counting, 25.7 mL, 28.8 mL and 32.09 mL of concentrated nitric acid were added to each 100 mL volumetric flask; then distilled water was added to the limit of the volumetric flask. Each flask is homogenized so that the nitric acid and distilled water are evenly mixed.

2.2 The process of forming Tin(II) Oxide

The synthesis process of SnO is carried out using the direct method. The raw materials used are tin powder and nitric acid. Tin powder is reacted with nitric acid at various concentrations of 4 M, 4.5 M, 5 M with a reaction volume of 19.8 mL, 17.5 mL, and 15.8 mL in a glass beaker under spontaneous stirring using a magnetic stirrer in various variations. Heating temperature is 100°C, 90°C, and 80°C with a holding for 2 hours until the brown gas is no longer visible in the glass beaker. The reaction between tin powder and nitric acid gives a yellowish precipitate. The samples are cooled at room temperature for 1 hour. The precipitate is washed using distilled water and acetone to remove acids until the pH of wash water is 6–7 which can be determined using litmus paper. Then the samples are dried at room temperature for 1 hour. The resulting sample is in the form of a coarse and dry powder which is then sampled in a mortar and filtered. Most of the samples were successfully tested using iodometry. The presence of Sn^{2+} is indicated by a color change in the sample and becomes the first evidence that the sample has been successfully formed. Then some of the samples were tested for thermal properties (DTA), morphology (OM) and phase composition (XRD).

3. Results and discussion

3.1 Iodometry test

To determine the oxidation state of the sample, the samples were analyzed for color change during the reaction.

Table 1 explains that the 4 M concentration gives an oxidation state of +2 for all variations in heating temperature, so that it becomes the first reference to confirm the success of the sample. The results of the iodometric test also confirm this concentra-

Table 1. Oxidation analyzed by iodometry test

Concentration	Time, h	Heating temperature		
		100°C	90°C	80°C
4 M	2	Sn^{2+}	Sn^{2+}	Sn^{2+}
4.5 M	2	Sn^{2+}	–	–
5 M	2	Sn^{4+}	Sn^{4+}	Sn^{2+}

tion. The optimum is at a concentration of 4 M with all heating temperatures. However, at a concentration of 5 M, the oxidation state was different. A concentration of 5 M at a heating temperature of 80°C gives an oxidation state of +2, while at a heating temperature of 100°C and 90°C, the sample turns into SnO_2 when the yellowish precipitate automatically turns into a white powder. This is evidenced by the iodometric titration test which gives an oxidation state of +4. Sergio et al. [4] reported that when heating the $SnCl_2{\cdot}2H_2O$ and HNO_3 materials with dilute nitric acid left in a closed container or desiccator for 2 months, a white precipitate adheres to the container. As the temperature rises, the white residue turns into a brownish residue with the formation of SnO_2. This indicates that SnO is not stable in all temperature ranges [5].

3.2 Thermal tests of *SnO with differential thermal analysis (DTA)*

Thermal tests with DTA were carried out to study the thermal properties of tin (II) oxide (SnO) with a concentration of 4 M at 80°C and a concentration of 5 M at 80°C. The sample with 4 M concentration at 80°C shows an endothermic phase in the range of 27°C to 61°C, and then thermal decomposition at 426°C. The sample with 5 M concentration at 80°C shows that the endothermic phase occurs in the range of 41°C to 231°C; then thermal decomposition takes place at 419°C. Exothermic reactions were not found for these samples, this is due to the decomposition of nitric acid that occurs by evaporation [19].

3.3 Morphology of *SnO using optical microscopy*

Optical microscopy (OM) characterization was carried out to determine the surface morphology of tin(II) oxide. The results of the surface morphology test at a magnification of ×500 are as follows.

The results show that the morphology of the sample is irregular; there is a residue of tin that does not completely react with nitric acid and also a yellowish color due to

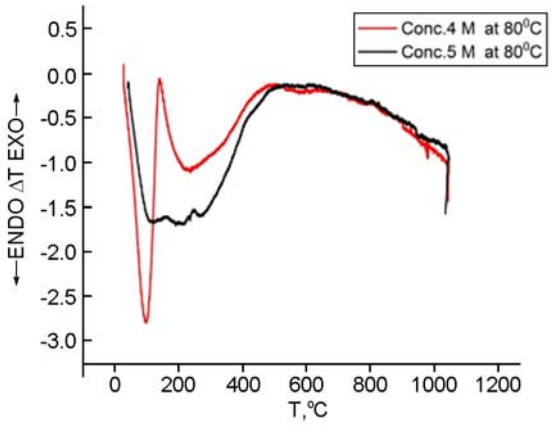

Fig. 1. Thermal tests of SnO by DTA.

Fig. 2. Microstructure image of SnO powder according optical microscopy, ×500.

the release of NO_2 when the sample is formed at room temperature [26].

3.4 X-ray Diffraction (XRD)

Analysis of the crystal structure and phases formed in the sample was carried out using X-Ray diffraction (XRD) using a device with radiation wavelength $\lambda = 1.5418740$ Å (Cu–Kα) operating at 40 kV and 30 mA. The diffraction pattern is shown in Fig. 3.

The diffraction pattern for the sample with 4 M concentration after heating at temperature of 100°C shows SnO with the main peak at $2\theta = 36.47$ degrees corresponding to the plane (002). The peak from the (316) plane and the formation of SnO_2 was identified in the sample at $2\theta = 26.62$, 33.24, 51.73 and 63.74 deg, respectively, corresponding to (110), (101), (211), and (112) planes. The diffraction pattern for the sample with 4 M concentration after heating at temperature of 80°C shows SnO, red-modified SnO, and the formation of SnO_2 at $2\theta = 26.72$, 33.25, 51.76 and 63.71 deg, re-

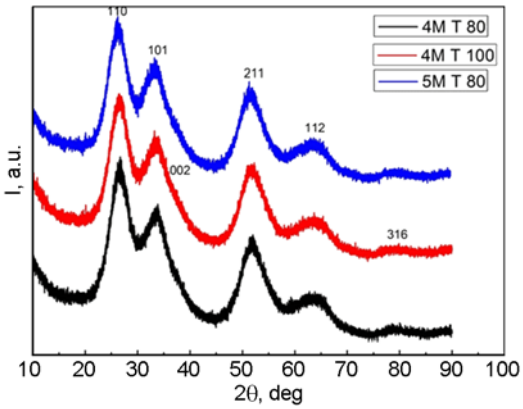

Fig. 3. SnO diffraction pattern.

spectively, for the planes (110), (101), (211), and (112). The diffraction pattern for the sample with 5 M concentration after heating at temperature of 80°C shows identified SnO, modified red-SnO and the formation of SnO2 at $2\theta = 26.71$, 33.21, 51.90, and 63.80 deg, respectively, for the planes (110), (101), (211), and (112). According to the XRD analysis, the samples with 4 M and 5 M concentrations with a heating temperature of 80°C did not have diffraction peaks for red-modified SnO and SnO. The authors (Fakhrutdinova et al., 2019) synthesized SnO using Sn granule and nitric acid at high temperatures, explaining that SnO was identified at one low intensity peak, namely $2\theta = 29.8$ deg, corresponding to (020) planes. In this study, black SnO was formed when the pH of the synthesized sample was above 5 [27] and red-modified SnO was formed with SnO_2 contamination [28].

Based on XRD analysis, the percentage of the composition of SnO is shown in the Table 2; the content of SnO for a concentration of 4 M with a heating temperature of 100°C is 22.4 %, the content of SnO for a concentration of 4 M with a heating temperature of 80°C is 31.4 and the content of SnO for a concentration of 5 M with a heating temperature of 80°C is equal to 20.7 %.

4. Conclusions

The process of forming SnO using tin powder and nitric acid has been successfully carried out by direct chemical reaction through iodometric titration. Based on the DTA, it was shown that the decomposition of the sample occurs at a temperature of 419°C for the sample with a concentration of 5 M with a temperature of 80°C and at 426°C and for the sample with a concentration of 4 M with a temperature of 80°C. The optical microscopy results show that the surface morphology is irregular. The XRD results identified SnO with a tetragonal crystal structure and SnO_2. Nitric acid concentration is very influential in ordering SnO. The concentration of concentrated nitric acid will easily stimulate the transition to SnO_2, and temperature fluctuations greatly affect the formation of SnO. This is because dilute nitric acid reacts very slowly with powder without releasing gas. So, the heating temperature is needed to speed up the reaction process, but too high heating temperature can accelerate the reaction to SnO_2.

Table 2. Phase analysis by XRD

Phases	Composition (%)		
	4 M, T = 100°C	4 M, T = 80°C	5 M, T = 80°C
SnO	22.4	31.4	20.7
SnO_2	38.3	41.3	50.9
SnO-red thermal modification	39.3	27.3	28.5

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