

Kinetics of the disproportionation of SnO

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Received 1 April 2004; received in revised form 2 June 2004; accepted 17 June 2004

Abstract

The kinetics of the disproportionation reaction of tin(II) oxide (SnO) to tin(IV) oxide (SnO₂) and tin metal (Sn) was studied ex-situ and in-situ by X-ray powder diffraction with synchrotron radiation. Depending on sample preparation and decomposition temperature, an intermediate oxide Sn₂O₃ was observed. From thermal disproportionation at different temperatures, we extracted the reaction rate law and the reaction rate coefficients k and activation energy E_A for the disproportionation of SnO and Sn₂O₃. The reaction follows a nucleation and growth mechanism according to Avrami-Erofeyev with a reaction exponent $m=2$. At low temperatures, a synchrotron radiation-induced disproportionation of SnO was observed.

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PACS: 61.10.Nz; 61.80.Cb; 82.30.Hk

Keywords: Disproportionation; Kinetics; Tin monoxide; Tin oxides; X-ray powder diffraction

1. Introduction

Due to its technological applications, SnO has received much attention. Powders of SnO can be used as anode materials in lithium rechargeable batteries, as coating materials or as effective catalysts for several acids [1]. The oxidation and disproportionation process of SnO thin films enables the production of thin SnO₂ films, which are used as transparent electrodes in liquid crystal displays (LCDs) and solar-electrical energy conversion devices or as chemical sensors [2].

SnO is blue-black and has the tetragonal litharge type structure (α -PbO, tP4, P4/nmm, SG No. 129, $Z=2$), while the colourless SnO₂ has rutile type structure (TiO₂, tP6, P4₂/mnm, SG No. 136, $Z=2$). SnO is metastable at ambient conditions and decomposes above a certain temperature with a noticeable rate into Sn and SnO₂. Depending on the

preparation method of the SnO and on the decomposition temperature, an intermediate oxide is found in various amounts. The crystal structure of this oxide is unknown and the disproportionation of SnO is the only known preparation method for this oxide.

One objective of this study was to find the best conditions for the synthesis of this intermediate tin oxide. To this end, the kinetics of the disproportionation reaction has been studied under various conditions. Ex-situ experiments were performed for an estimate of the reaction times and also for the very slow reactions at low temperatures. In-situ experiments were used to get more detailed information about the reaction process.

There is still no conformity about the correct chemical formula of the intermediate oxide. Where various authors use the chemical formula Sn₃O₄ [3–6] proposed by [7] and [8] the chemical analysis from [9] and [10] show that the correct formula is Sn₂O₃. Unfortunately, these last two papers have not found much attention. Our chemical analysis [11] also confirms the chemical formula Sn₂O₃ for the intermediate oxide.

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2. Experimental

SnO from two different suppliers has been used for this study. Sample CU obtained from Chempur with purity 99.9% and 100 mesh has a blue-black metallic lustre. Sample AU obtained from Aldrich with purity 99+% and grain size <40 μm is a black metallic powder. From the untreated materials CU and AU, the ground samples CG and AG were obtained by grinding under nitrogen atmosphere. In both cases, a pale-brown mat powder was obtained. The change of colour and lustre can be attributed to the roughening of the crystallite surface during grinding [12]. Microscopic inspection of the ground samples yielded an average grain size of 1–2 μm . Sample CG has been used for the in-situ kinetic studies.

For the ex-situ studies about 0.5 g of the sample material were encapsulated in evacuated (10^{-5} mbar) quartz tubes and heated in an oven at the given temperature. After the stated reaction time, the ampoules were quenched in water. The samples such obtained were fixed on tape and investigated by energy dispersive X-ray powder diffraction (EDXRD) in order to obtain the composition of the reaction products. The EDXRD studies were carried out at station F3 of HASYLAB/DESY with white synchrotron radiation with a critical energy of 16 keV from a bending magnet at the DORIS-III storage ring with a positron energy of 4.5 GeV. Further details about kinetic studies at beamline F3 can be found in Ref. [13].

For the in-situ studies, a heated diamond anvil cell (DAC) made of a titanium alloy has been used as reaction vessel chosen for two reasons: first, it prevents oxidation of the sample by oxygen from air and, second, it provides comparable conditions to other experiments, which have been performed under high pressure in the DAC [14]. The temperature was controlled by a PID temperature controller with a thermocouple fixed to the DAC. The heating rate for this setup is about 100 $^{\circ}\text{C}/\text{min}$ with a maximum temperature of about 500 $^{\circ}\text{C}$.

The X-ray powder diffractograms were evaluated with the computer program EDXPOW [15]. Individual Gaussian profiles were fitted to the diffraction peaks. The Sn-K β_1 X-ray fluorescence line serves as internal intensity standard for the diffraction intensities.

3. Results and discussion

The disproportionation reaction of SnO has been investigated by ex-situ and in-situ experiments. The ex-situ experiments were performed in order to obtain an estimate of the reaction rates and the decomposition products formed by the disproportionation reaction of SnO depending on temperature, reaction time and starting material. The in-situ experiments provide much more detailed information on the reaction progress, in particular for fast reactions.

The composition of the sample is determined from the intensities of the diffraction lines. The content of metallic Sn could not be determined directly in-situ by X-ray diffraction because tin is liquid at reaction temperatures above 232 $^{\circ}\text{C}$.

However, the content of Sn is given by the stoichiometry of the disproportionation reactions:



For simplicity, we use the following equivalents:



With these equivalents, we can rewrite the chemical reactions (1)–(3) to



During the disproportionation, the equation

$$[A] + [B] + [C] = 1 \quad (10)$$

always holds for the concentrations [A], [B] and [C] of the components and the reaction progress α is given by

$$\alpha = 1 - [A] = [B] + [C] \quad (11)$$

The contents of A, B and C has been determined from the intensity of typical diffraction lines of the corresponding constituents SnO, Sn $_2$ O $_3$ and SnO $_2$ with respect to the intensity of the Sn-K β_1 X-ray fluorescence. Some typical spectra are shown in Fig. 1. For the components A and C, the diffraction to fluorescence intensity ratio has been determined from pure SnO and from a fully decomposed sample, respectively. For component B, this ratio has been determined from various samples with high content of B using Eq. (10) for the correction of the minor contents of A and C. The estimated uncertainty in the composition determination including overlapping diffraction lines and texture effects of the samples is less than 10%. This method has also been used for the ex-situ experiments because the content of Sn could not be well determined due to the coarse

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