



# A study of a reduction of a micro- and nanometric bismuth oxide in hydrogen atmosphere

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## ABSTRACT

A reduction of bismuth oxide in hydrogen atmosphere was investigated. The reaction was performed with a material in various structural forms: powder: with micrometric grains, powder with nanometric grains and powder pressed into pellets. The process was performed in both isothermal and non-isothermal conditions. An activation energy of the reaction calculated with Friedman method was found to be about 85 kJ/mol for the reduction of both micrometric powder and pellets. A model fitting analysis based on Coats-Redfern method suggests, that the reaction is limited by a diffusion of gaseous reactants, what is consistent with a structural analysis. An effect of liquid bismuth evaporation was noticed at the beginning of the process. This phenomenon was much stronger in the case of reduction of nanometric powder. The activation energy was estimated to be about 30–50 kJ/mol. The reaction could have been performed at lower temperature.

## 1. Introduction

A reduction of metal and metalloid oxides in reducing atmospheres is a way of producing metals and intermetallic alloys and compounds, especially advantageous when elements have different melting points [1]. Reduction with hydrogen is also a method to regenerate metallic catalysts, e.g. in carbon nanotubes synthesis [2].

Most of the investigations concerning reduction with hydrogen have been done on transition metal oxides, like e.g. iron [3–5], nickel [6–9], silver [10] copper [11] or molybdenum [12,13]. Typically, thermogravimetric analysis is performed in order to determine an extent of the reaction. Using small amount (10–30 mg) of powder forming a thin layer on a microbalance helps to exclude the influence of diffusion outside grains [4,6,12]. Experiments can be performed in isothermal or non-isothermal (usually with constant heating rate, up to 30 K/min [11]) conditions. For measurements in isothermal conditions, instantaneous gas change in apparatus is required at particular temperature [12]. For this reason, non-isothermal experiments are easier to conduct and more popular.

Methods of kinetic data analysis are well explained by S. Vyazovkin's et al. [14,15]. Additionally, a list of functions describing different reaction mechanism gathered in [6] is helpful. Using different methods of kinetic calculations for the same experimental data can lead to different results [10,11]. Moreover, in non-isothermal experiments, many different functions can be fit to the experimental data, provided

that other kinetic parameters can be freely adjusted during fitting [14]. For isothermal measurements a fitting procedure is more simple and can be performed more accurately. Also differences in structure of the oxide – grains' size, crystal structure defects [3], as well as form of the sample (e.g. powder, pellet) can significantly change a mechanism of the reaction [7]. This induces many difficulties in comparing different studies. In case of the oxide reduction analysis, a Friedman method is applied for the activation energy calculation [4–6,10]. For the evaluation of the reaction model function, a Coats-Redfern method can be used [3,6,10,13].

An influence of grains aggregation on the reduction process has been investigated for nickel oxide pellets [7] and wires [8]. Data obtained for reduction of pellets was successfully fitted to a “structural model” based on grain sizes as well as on a size and distribution of pores. Additionally, photographs of pellets after partial reaction confirmed a prediction based on the proposed model and a key role of mass transfer. This can be compared to a study of NiO powder reduction [6], which revealed nucleation and growth of Ni particles as a rate-determining step. Investigation of reduction of NiO wires [8] also has shown a significant role of diffusion, however, authors pointed, that at low temperatures (up to 800 K) the rate of grains nucleation and growth is also significant. Kinetic data analysis was supported by SEM imaging with chemical composition analysis. A porous structure was found in partially reduced areas of samples. Ni phase was identified around pores and NiO and bulk areas, again confirming an influence of a mass

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transport in the reaction kinetics.

A reduction of bismuth oxide was investigated by F. Korkmaz et al. [16]. The reaction was conducted with ethanol, decomposing into hydrogen and carbon oxide. That study revealed, that in a low temperature range the reaction rate is limited by kinetics of the reaction itself (nucleation and growth of liquid bismuth particles), while at high temperatures (above 700 K) by a transport of gaseous reactants through the powder bed. It was found, that Bi forms a layer on the surface of  $\text{Bi}_2\text{O}_3$  particles, which transforms into micrometric Bi droplets growing to millimeters while reaction proceeds. Other study [17] shown that at temperatures lower than 500 K the reaction rate is limited by a transport in a gaseous phase. The reduction of  $\text{Bi}_2\text{O}_3$  is a single step reaction (no other Bi oxides were found to be stable), however calculations show a possibility of gaseous bismuth hydrides formation. The reduction of bismuth ions by hydrogen in bismuth silicate and germanate glasses has also been previously investigated [18,19]. It was found, that Bi clusters, with diameters up to 10 nm, are formed in a glass matrix in a layer under the glass surface. Thickness of this layer was found to be 40–50  $\mu\text{m}$ . A migration of Bi atoms to the surface and formation of spherical particles was also noticed. In our previous research a method of oxides reduction with hydrogen has been applied for a synthesis of thermoelectric materials, see [20,21] and references therein. Similar method was applied by Lee et al. for bismuth telluride based materials [22–24]. These studies focused on parameters of the synthesis procedure and properties of materials rather than on the reaction itself. Only “external” factors, like time and temperature have been investigated, without an insight into “internal” reactions mechanisms. In order to investigate the reduction process we decided to firstly investigate an influence of a structure of substrates on the reaction course.

In this study, a reduction of bismuth oxide with hydrogen  $\text{Bi}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Bi} + 3\text{H}_2\text{O}$  is investigated in isothermal and non-isothermal conditions. The reaction is conducted for different forms of the bismuth oxide – micrometric sized powder, the same powder pressed into pellets as well as a ball-milled nanopowder. The results will provide an information about how the form of the oxide influences reaction processes. It is expected, that the higher surface area will enhance kinetics of the reaction. This knowledge will be helpful in designing procedures of materials synthesis with an oxide reduction method. Reaction extent is measured by a thermogravimetry method. Results of the data analysis are compared with SEM images of reaction’s products at different stages of the reaction.

## 2. Experimental

In order to investigate mechanisms of the reduction of bismuth oxide, thermal gravimetric measurements have been conducted in non-isothermal and isothermal conditions. A custom made experimental setup is presented in Fig. 1. A reduced material was put into stainless steel crucible lined with an aluminium foil. The crucible was placed on the top of a stainless steel rod, transferring load onto a balance (AXIS ALZ120), measuring with a 0.0001 g accuracy. Thermocouple placed inside of the rod measured temperature on its top with a maximum uncertainty equal to 1.6%. A whole apparatus was hermetically closed for the experiments. Tube furnace was used to increase the temperature

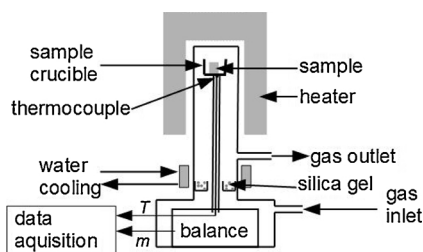


Fig. 1. Scheme of experimental apparatus.

of the reaction chamber. A lower part of the column was cooled with water. Additionally, silica gel was put in the cooled area of the chamber for capturing of water vapour.

Investigation was performed with a bismuth oxide powder from Alfa Aesar (99.975%). For experiments with material further called a “powder” it was used without an additional processing. For measurements of a reduction of pellets, the powder was pressed under 520 MPa uniaxial pressure in cylindrical matrix with a diameter of 6 mm. A mass of a reduced material was about 0.85 g in each measurement. Additional experiment was performed with a powder milled in a planetary mill (further called “nanometric powder” or “nanopowder”). SEM images of both powders are provided in Supplementary Information, Figure S1. After closing the apparatus, it was rinsed with nitrogen in order to remove air. After that, the reaction chamber was rinsed with a rapid stream of hydrogen. After rinsing the experiment was started with turning the heater on and a constant 160 ml/min flow of hydrogen was kept. Mass and temperature measurements were performed every 10 s until the mass changes stopped. In order to fabricate the partially reduced samples, the reaction was interrupted when a mass change reached an appropriate value – heater was removed, chamber was rapidly rinsed with nitrogen (hydrogen flow was stopped) and cooled down with a fan. In order to verify results of calculations and to perform low temperature experiments, isothermal reactions were also performed. In these processes the apparatus with sample was heated to the experimental temperature in nitrogen atmosphere. Then, the reaction chamber was rapidly rinsed with hydrogen for about 5 min. After that, the gas flow was decreased to the constant value of 160 ml/min and the measurement was started.

Structural investigations of the materials were performed. X-Ray diffraction patterns were obtained with a Philips X’Pert Pro MPD diffractometer. Electron microscopy was done with a FEI Quanta FEG 250 microscope with a secondary electron detector. Elemental analysis was performed with Energy Dispersive X-ray Spectroscopy with an ApolloX SDD detector. Accelerating voltage was 10 kV for imaging and 30 kV for EDS. Surface area of the milled powder was measured with BET analysis using Quantachrome NOVAtouch 1LX instrument at 77 K. Surface area of the other materials was too low to be measured.

## 3. Methods of data analysis

Experimental data was limited to a region of actual reaction (changing mass). Reaction extent  $\alpha$  was calculated according to eq. 1, where  $m_0$  is initial mass of sample,  $m(t)$  – measured mass,  $m_{ox}$  – mass of oxygen in initial  $\text{Bi}_2\text{O}_3$  sample.

$$\alpha = \frac{m_0 - m(t)}{m_{ox}} \quad (1)$$

Reaction rate is described by equation 2, where  $A$  is pre-exponential constant,  $E$  – activation energy,  $R$  – universal gas constant and  $f$  – function describing reaction model [11]:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (2)$$

Dependence of  $\alpha$  on time ( $t$ ) was approximated by the 7<sup>th</sup> order polynomial denoted as  $\alpha_c$ . Correlation coefficient  $R^2$  values were at least 0.9995, lower values were obtained for micrometric powder (at least 0.999). Reaction rate ( $d\alpha_c/dt$ ) values were simply obtained from  $\alpha_c(t)$ .

Supposing that function  $f$  is independent from  $T$  and  $\alpha$  is constant, a linear relation of  $\ln(d\alpha_c/dt)$  on  $1/T$  can be derived from eq. 2:

$$\ln \frac{d\alpha_c}{dt} = \ln [A f(\alpha)] - \frac{E}{RT} \quad (3)$$

Friedman method to calculate activation energy involves a linear regression of a reaction rate and temperature data according to eq. 3. This method was used to calculate  $E$  for the reduction of different forms

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