



A kinetic study of copper(II) oxide powder reduction with hydrogen, based on thermogravimetry

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ABSTRACT

The reduction of powdery copper(II) oxide was carried out in a stream of gaseous mixture 25% H₂ + Ar, and followed by thermogravimetry. The two samples of different history were studied: the commercial one, and that synthesized by citrate gel combustion method. The characterization of the starting materials, based on X-ray diffractometry and scanning electron microscopy, indicated equal crystal structure, but different particle size and morphology. The particle size and shape of the metallic particles obtained upon the reduction were observed by means of electron microscope. By a nonlinear regression analysis by means of a software Kinetics05, the experimental data were fitted with the nucleation-growth kinetic model, and the corresponding kinetic parameters were determined.

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1. Introduction

Copper(II) oxide is known as a catalyst important in many chemical reactions that involve hydrogen, such as methanol synthesis from CO or CO₂ [1,2] oxidative methanol reforming [3], NO reduction, etc. [1,4]. Also, it is very active in carbon monoxide oxidation reaction [5,6] being important in the treatment of automobile exhaust gases. Recently, its activity was reported to be enhanced by a zirconia support [7].

The knowledge about the reduction of CuO in reduction gas atmosphere is interesting from several aspects. The kinetics of reduction is connected to the stability of catalytic activity of CuO [5–7]. Mixtures of CuO_x/Cu are utilized for the fabrication of components in the microelectronic industry [8]. Recently, the reduction of mixture of CuO with refractory metal oxides, for instance WO₃ [9–11] was considered as a method to obtain metal composites having both high hardness and electric conductivity.

Although the studies of CuO reduction relate commonly to the procedures involving the heating in hydrogen atmosphere, this process is generally not well understood. Some authors established that during the reduction of CuO under particular conditions, one may track all of the copper oxide forms in the series CuO–Cu₄O₃–Cu₂O–Cu [12,13]. Kim et al. [14], by using

synchrotron-based high-resolution *in situ* X-ray diffraction (S-XRD) techniques revealed that CuO in single-step reduces to metallic Cu (Cu²⁺ → Cu⁰), if the hydrogen flow is set on more than 15 mL min⁻¹, however, at gas flow rate less than 1 mL min⁻¹, formation of Cu₂O was evidenced. Fernandez-Garcia et al. [15] showed by means of temperature-programmed reduction that the reduction process of CuO involves either two or three intermediate species. Based on the *in situ* X-ray diffraction studies of CuO reduction, Vong et al. [16] and Rodriguez et al. [17,18] came to the opposite conclusions about the appearance of intermediate compounds.

From the available literature it follows that the studies of reduction of both supported and unsupported CuO were focused on the detection of intermediate species [12–18], but rarely on very kinetics of the process [19]. The present paper reports about the study of the kinetics of reduction of unsupported CuO by hydrogen, based on thermogravimetric measurements. The recently accepted multi-constant-heating rate procedure [20,21], and nucleation-growth reaction model were used to interpret the experimental data. To consider the effects of sample history, the CuO probes from different sources were considered: the commercial one and the one synthesized by citrate gel combustion method.

2. Experimental procedure

2.1. Materials

A stock, commercial (Kemika, Zagreb) CuO (>99%) sample, assigned as C sample, upon its characterization by XRD and SEM

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methods described below, was used as purchased. The chemicals used for citrate gel combustion synthesis of CuO were copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and citric acid, $\text{C}_6\text{H}_8\text{O}_7$ (Merck p.a.). Both components were dissolved in water in the concentration of 1 M, and the solutions were mixed to obtain mole ratio of nitrates against citric acid of 3.6, enabling a complete combustion of organic constituent [22] regardless of the exposition to air. The solution was heated in an open glass beaker to evaporate water until a solid homogeneous transparent gel remained, tightly adhered to the beaker walls. The heating was then continued in an open oven up to the temperature of approx. 300 °C, when a self-ignition happened, yielding CuO in a form of black powder. To remove the residues of carbon, the powder was additionally heated in air at 450 °C during one half of hour.

2.2. Thermal analysis

The reduction of CuO samples was estimated by simultaneous thermogravimetry and differential thermal analysis, under flow of 25% $\text{H}_2 + \text{Ar}$, at a flow rate 80 mL min^{-1} . The purity of gases was 99.995 vol.%. The device used for thermogravimetric measurements was TA SDT Model 2060. Different heating rates in the interval $2.5\text{--}30 \text{ }^\circ\text{C min}^{-1}$ were used.

2.3. Electron microscopy

The particle size and morphology of CuO powders, and the Cu particles obtained by CuO reduction were observed by scanning electron microscope (SEM) JEOL JSM-6390 LV.

2.4. X-ray diffractometry

The X-ray diffractograms of the CuO samples were obtained by means of Philips PW-1050 automatic diffractometer with a $\text{Cu K}\alpha_{1,2}$ line of 1.5418 nm.

2.5. Kinetic analysis

The starting equation of thermal analysis is usually written in a form which assumes an Arrhenius expression for the rate constant:

$$\beta \frac{d\alpha}{dT} = A e^{-E_\alpha/RT} f(\alpha) \quad (1)$$

where α is the fraction reacted (alternatively called conversion degree), T is the temperature, β is the heating rate ($\beta = dT/dt$, where t is the time), A is the pre-exponential factor, E_α is the activation energy, R is the gas constant and $f(\alpha)$ is the differential form of the reaction model, i.e. a function of α which in best way fits the experimental data.

The kinetics analysis was performed by means of Software Kinetics05 [23], which includes majority of reaction models, ranging from 1st order, n th order, nucleation-growth model, as well as the activation energy distribution models, and uses a non-linear regression methods to determine the parameters of Eq. (1) to fit in a best way the experimental data.

To check the presumed invariance of E_α on α , the software Kinetics05 performs the isoconversional “model-free” analysis by means of expanded Friedman [24,25] and modified Coats–Redfern [25,26] multi-heating rate methods:

The expanded Friedman method is based on the logarithm of Eq. (1):

$$\ln \left(\beta \frac{d\alpha}{dT_\alpha} \right) = -\frac{E_\alpha}{RT_\alpha} + \ln(A(1-\alpha)) \quad (2)$$

where T_α , E_α and A are the time, temperature, apparent activation energy and pre-exponential factor, respectively at a common

fraction reacted, α . The ratio $-E_\alpha/R$ is the slope and the addend $\ln\{A(1-\alpha)\}$ may be determined as the intercept with vertical axis of the plot of $\ln(\beta d(1-\alpha)/dT_\alpha)$ vs. $1/T_\alpha$.

The modified Coats–Redfern method [25], a multi-heating rate application of the Coats–Redfern equation, expressed by the equation:

$$\ln \left[\frac{\beta}{T^2(1-2RT/E_\alpha)} \right] = -\frac{E_\alpha}{RT} + \ln \left(-\frac{AR}{E_\alpha \ln(1-\alpha)} \right) \quad (3)$$

is similar more to the FWO (Flynn, Wall, Ozawa) method [27,28] than to the original single-heating-rate Coats–Redfern method. At a fixed conversion degree, for each of the heating rates (β), assuming in the first attempt that $RT/E_\alpha = 0$, a plot of the left-hand side of Eq. (3) against $1/T$ yields a straight line of the slope $-E_\alpha/R$, which enables to obtain the starting value of E_α for actual value of α . This value is then used for the next iteration, and after several iterations a constant value E_α may be achieved. It may be further substituted into the intercept of the plot of Eq. (3) to obtain A . By changing α in steps, a series of relating E_α values may be determined.

The function $f(\alpha)$ (reaction model) is not included in the slope-determining term of Eqs. (2) and (3), and thus does not influence the value of E_α what justifies somewhat the use of the term “model-free” methods. However, in order to extract the value A from the intercepts of the plots of Eqs. (2) and (3), the form of $f(\alpha)$ should be specified, and, as already mentioned, Kinetics05 uses automatically first-order function: $f(\alpha) = (1-\alpha)$ for this purpose. If the system under consideration obeys the first-order reaction model, then the values A and E_α do not depend on α . However if a strong dependence of E_α on α is observed, one must seek another kinetic model to describe the experimental results.

The Kissinger method [29,30] is a special isoconversional model-free case of determining A and E_α . It implies a series of experiments at different heating rates β and plotting $\ln(b/T_{\max}^2)$ vs. $1/T_{\max}$ where T_{\max} means such temperature at which, for a given heating rate, the reaction rate passes the maximum. The slope of such plot is $-E_\alpha/R$, almost regardless on the reaction order. This diagram may be plotted manually, using the temperatures of maxima of reaction rate either determined experimentally, or calculated by the software, for various heating rates. For this purpose we used the rate maxima determined by the software, which according to Fig. 6a and b practically overlap with the experimental ones.

The Prout–Tompkins (P–T) model used originally by the authors to describe the decomposition of potassium permanganate [31], was extended by Burnham [23], by introducing the exponents n and m , different than one, to read:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n(1-q(1-\alpha))^m \quad (6)$$

where q is a fixed parameter, and n and m are adjustable to achieve the best fit to the experimental data. The coefficient q , being only slightly less than one, provides to obtain nonzero reaction rate at $\alpha = 0$ [25]. This model is applicable to a wide range of solid-state processes involving the nucleation and growth. If $n = 0$ and $m = 1$, Eq. (6) has the limit of linear chain-branching model, usable for instance in the polymer degradation. If $n = 1$ and $m = 0$ it has the limit of a first-order reaction. The case $n = m = 1$ gives the standard Prout–Tompkins model [31]. As mentioned by Burnham [32] and Brown [33], the sigmoidal course of α vs. time function that corresponds to this model, is very similar to the same course predicted by the Avrami–Erofeev model [34–36] (developed to describe nucleation and growth process during the phase transformations), and practically overlaps with the two-parameter Šesták–Berggren model [37,38] (in which the Avrami parameter p is set to zero) [32]. Thus, extended P–T model (Eq. (6)) may be used to simulate the nucleation-growth processes in solids.

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