

Reduction of SnO₂ with Hydrogen

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This study deals with the reduction of tin oxide by hydrogen in the temperature range of 773~1023 K and the hydrogen partial pressure of 30.4~101.3 kPa. It aims to investigate the kinetics of the reaction between tin oxide and hydrogen. The hydrogen reduction of tin oxide is to be related with the efforts to extract tin metal with decreasing the emission of carbon dioxide which causes global warming. The experiments were carried out under isothermal condition in hydrogen atmosphere using TGA equipment. The reduction rate of tin oxide to tin metal by hydrogen was found to be relatively fast under the whole conditions until the reduction ratio of SnO₂ approaches to about 0.95. As an example, at 1023 K under a hydrogen partial pressure of 101.3 kPa, almost 100% of tin oxide was reduced to tin metal in 10 min. The nucleation and growth model yielded a satisfactory fit to these experimental data. The reaction was first order with respect to hydrogen partial pressure and had an activation energy of 62.5 kJ/mol (15.0 kcal/mol). [doi:10.2320/matertrans.M2011118]

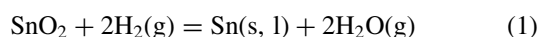
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1. Introduction

In the conventional smelting of tin, large amount of carbon dioxide together with tin metal is inevitably emitted from the two stage carbothermal reduction operation of tin oxide (cassiterite) concentrate because carbon is the main energy source and the reducing agent used in the tin smelting.¹⁻³⁾ At the present time, approximately 2 tonnes of carbon dioxide are reported to be generated for the production of 1 tonnes of tin metal.⁴⁾ In general, the carbon dioxide is well known to be a major gas of the greenhouse gases. Thus, a diminution in carbon dioxide emission from the processes after the Kyoto agreement has been strongly required. In the tin smelting, the only solution is to use hydrogen and electricity obtained without using fossil fuels instead of carbon in the tin making.

From such a viewpoint, the reduction reaction of SnO₂ by hydrogen is of interest as a means of diminishing carbon dioxide emission in the tin smelting processes. The reduction reaction can be represented by



The standard Gibbs free energy change (ΔG°) and equilibrium constants (K_1) of the reaction (1) are summarized in Table 1 using HSC Chemistry 5.1 (A. Roine, Outokumpu, 2002) version. The table indicates that the reaction (1) is favorable thermodynamically under the considered temperature range between 823 and 1023 K.

In the present research, a kinetic study on the hydrogen reduction of tin oxide was experimentally investigated under isothermal condition using TGA equipment. The kinetics of the reduction reaction would offer fundamental data to understand the influence of employed conditions such as temperature and hydrogen partial pressure on the smelting process of tin.

2. Experimental

Experiments were performed in a typical thermogravimetric analysis (TGA) apparatus similar to the one described

Table 1 ΔG° and K_1 values of the reaction (1).

Temp. (K)	ΔG° (kJ/mol)	K_1
673	3.83	0.06
773	1.22	0.45
873	-1.28	2.10
973	-3.70	6.79
1073	-6.05	17.03
1173	-8.32	35.46

in detail elsewhere.⁵⁾ The TGA apparatus consisted of a recording microbalance from one arm of which a shallow silica tray for sample was suspended by a platinum chain into a reactor tube located within vertical tubular furnace. The reactor tube was an Inconel tube of 5.0 cm inner diameter and 65 cm length. The microbalance continuously recorded the mass changes taking place during the reaction. During the experiments, the balance was purged with argon gas to prevent the intrusion of reacting gas and hot gases. Powder samples weighing 690~710 mg placed in a shallow holder were used for each run. In order to measure the rates of the hydrogen reduction of SnO₂ in the negligible level of external mass transfer effects, sufficiently high flow rate (11.7 mL/s) of hydrogen and bed height (below 1 mm which is obtained by spreading 700 mg of SnO₂ powders as a thin layer on a shallow sample tray) were chosen through preliminary experiments.

Hydrogen (99.9%) and argon gases (99.9%) were supplied by Air Products Company in Korea. SnO₂ powder (99.9 mass%) of -45 μm size obtained from Aldrich Chemical Co. was used as a raw material.

3. Results and Discussion

Rate measurements for the hydrogen reduction reaction of tin oxide powder were carried out at temperature ranges between 773 and 1023 K under hydrogen partial pressures between 30.4 kPa and 101.3 kPa. The experiments were continued until the solid sample showed no noticeable further

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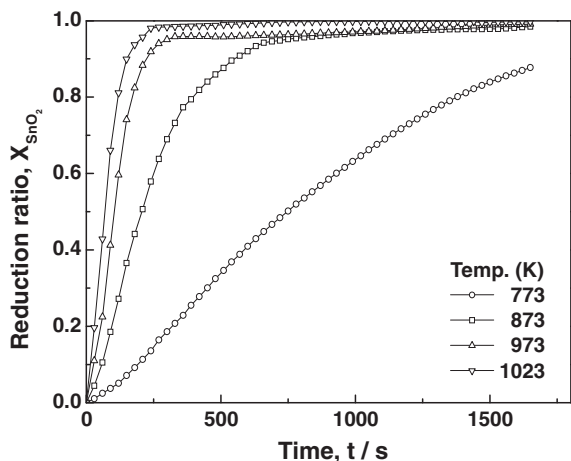


Fig. 1 Effect of reaction temperature on the reaction rate of H₂-SnO₂ under a hydrogen partial pressure of 101.3 kPa.

mass change. Fractional reduction ratio at a particular time was determined by dividing the weight change of the solid sample up to that time by the total weight change at complete reaction calculated from the stoichiometry of reaction (1).

3.1 Effect of the reaction temperature

The effect of reaction temperature on the hydrogen reduction rate of SnO₂ powder was determined by varying the reaction temperatures between 773 and 1023 K at a fixed hydrogen partial pressure of 101.3 kPa, while all other experimental variables, such as sample mass and gas flow rate, were nearly identical for the measurement. Figure 1 shows the effect of reaction temperature on the reduction of tin oxide powder by hydrogen. The reduction ratio-time curves shows that the reaction has a short initial induction period followed by a constant and rapid period. These curves were reproducible within ± 4 pct at each temperature. At 1023 K and a hydrogen partial pressure of 101.3 kPa, almost 100% of tin oxide was reduced to tin metal in 10 min.

3.2 Effect of the hydrogen partial pressure

The effect of hydrogen partial pressure on the H₂-SnO₂ reaction rate was measured by varying the hydrogen partial pressure between 30.4 kPa and 101.3 kPa in an argon atmosphere at a fixed reaction temperature of 873 K. This was done by varying the flow rates of argon and hydrogen gases while maintaining the total flow rate at 11.7 mL/s. Figure 2 shows the effect of hydrogen partial pressure on the hydrogen reduction reaction of tin oxide at 873 K. These curves show that the reduction rate increases moderately with increasing hydrogen partial pressure and over 98% of tin oxide is reduced to tin metal in 27 min at 873 K under a hydrogen partial pressure of 101.3 kPa. It was also shown in the figure that the reduction ratio-time curves has an initial induction period followed by a constant and rapid period as observed in the effect of reaction temperature on the reaction (see Figs. 1 and 2).

3.3 Interpretation of the rate data

The reduction of tin oxide by hydrogen gas under the considered experimental conditions is a gas-solid reaction

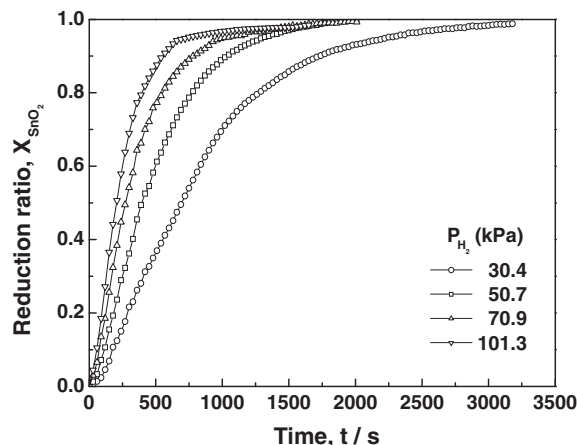


Fig. 2 Effect of hydrogen partial pressure on the reaction rate of H₂-SnO₂ under a reaction temperature of 873 K.

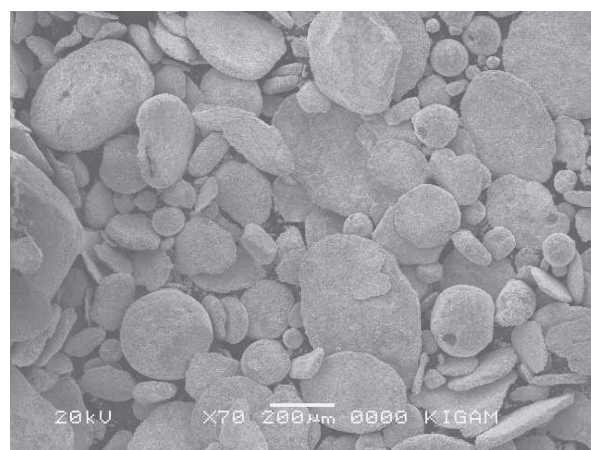


Fig. 3 Scanning electron microscopy (SEM) picture of the tin metal phase produced after the reaction at a reaction temperature of 1023 K under a hydrogen partial pressure of 101.3 kPa.

in which molten tin is formed. Figure 3 shows scanning electron microscopy (SEM) picture of the tin metal phase produced after the reaction. The molten tin might form around the particles and inhibit subsequently gaseous transport during the reaction. It was thus expected that the reaction rate is initially rapid and leveled off at less than the complete reduction because of pores being plugged by molten tin. However, such phenomena were not investigated from the rate data of the reaction as shown Figs. 1 and 2. This might be the reason that the rate of the hydrogen reduction reaction of tin oxide is relatively fast until the reduction ratio is about 0.95. Also, the figures indicate that the reduction rate has an initial induction period followed by a constant and rapid period. This is a typical feature of nucleation and growth processes. Thus, the nucleation and growth model is expected to best represent the reaction of tin oxide powder with hydrogen, which was verified after trying a number of different rate expressions such as the pore blocking model, the spherical shrinking-core model, and the power law. On the other hand, several researchers reported that the nucleation and growth model was found to fit the hydrogen reduction reaction rate of metal oxides.^{6,7)}

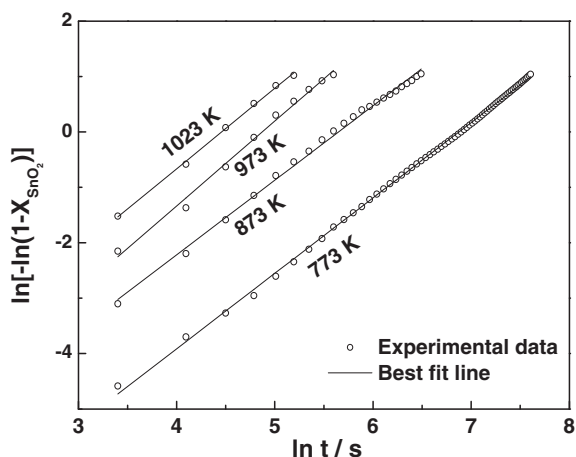


Fig. 4 Plots of $\ln[-\ln(1 - X_{\text{SnO}_2})]$ versus $\ln t$ using the rate data of Fig. 1 according to eq. (2).

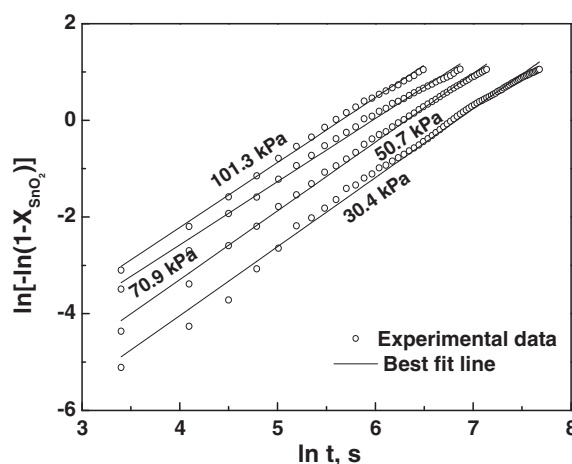


Fig. 5 Plots of $\ln[-\ln(1 - X_{\text{SnO}_2})]$ versus $\ln t$ using the rate data of Fig. 2 according to eq. (2).

In the kinetic analysis using the nucleation and growth model, the degree of reduction ratio of SnO_2 by hydrogen gas until 0.95 was analyzed. In this rate expression, the reduction ratio of SnO_2 to Sn is related to the reaction time by⁸⁾

$$[-\ln(1 - X_{\text{SnO}_2})]^{1/m} = k_{\text{app}} \cdot t \quad (2)$$

where X_{SnO_2} is the reduction ratio of SnO_2 , m is a constant, k_{app} is the apparent rate constant (s^{-1}), and t is the reaction time (s) which is given by

$$k_{\text{app}} = b \cdot k \cdot f(p_{\text{H}_2}) = b \cdot k \cdot p_{\text{H}_2}^n \quad (3)$$

Here, b is the stoichiometry constant ($b = 1/2$ in this system, according to the formulation of Sohn⁹⁾) for the reaction (1), k is the intrinsic rate constant ($\text{s}^{-1} \cdot \text{kPa}^{-n}$), p_{H_2} is the hydrogen partial pressure (kPa) in the bulk gas, f designates the partial pressure dependence of the rate, and n is the reaction order for the partial pressure of hydrogen gas. It is apparent from eq. (2) that a plot of $\ln[-\ln(1 - X_{\text{SnO}_2})]$ against $\ln t$ should be linear with m as the slope and $m \ln k_{\text{app}}$ as the intercept for $\ln t = 0$.

The validity of the nucleation and growth model rate expression for the hydrogen reduction reaction of tin oxide powder was verified by first plotting the reduction ratio-time curves of Figs. 1 and 2 according to eq. (2), as shown in Figs. 4 and 5. Examination of these figures reveals that the rate data follow well eq. (2). In these Figs. 4 and 5, the values of the slopes were calculated by regression analysis. The straight lines with high-correlation coefficient ($r > 0.993$) were selected to represent the possible controlling mechanism. The best-fit values of m at different hydrogen partial pressures and temperatures totaling seven runs varied between 1.31 and 1.53. The use of a single value of m for the same material is consistent with the mechanistic justification for the use of the nucleation and growth kinetics equation, and thus all of the calculated lines were plotted with an average value of m to be 1.41.

In order to evaluate the hydrogen partial pressure dependence of k_{app} , the values of k_{app} thus obtained from the intercepts are plotted in Fig. 6 against the hydrogen partial pressure. As shown in Fig. 6, a straight line through the origin is obtained, which indicates a first-order reaction with

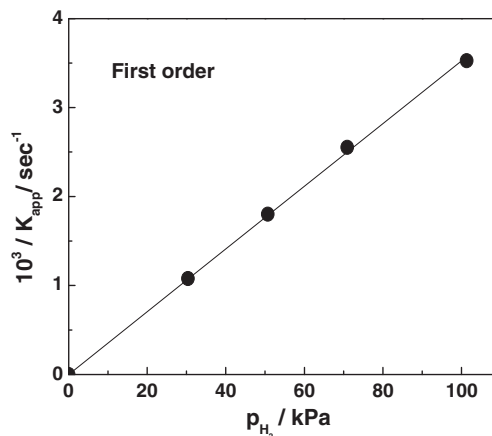


Fig. 6 Dependence of the apparent reaction rate constant on the partial pressure of hydrogen from the results shown in Fig. 2.

respect to the hydrogen partial pressure in a mixture with argon. Thus, eq. (3) can be rewritten as

$$k_{\text{app}} = b \cdot k \cdot f(p_{\text{H}_2}) = (1/2) \cdot k \cdot p_{\text{H}_2} \quad (\text{s}^{-1}) \quad (4)$$

The values of the rate constant, k , were obtained from eq. (4) at various temperatures and plotted in Fig. 7. Figure 7 is an Arrhenius plot of the intrinsic rate constants. The slope of the straight line placed through the experimental points corresponds to an activation energy of 62.5 kJ/mol (15.0 kcal/mol). The line through these data can be expressed by the following equation:

$$k = 3.52 \times 10^{-1} \cdot \exp[-7517.1/T] \quad (\text{s}^{-1} \cdot \text{kPa}^{-1}) \quad (5)$$

Using eq. (5), the reaction rate of the hydrogen reduction of tin oxide powder is thus represented by the following equation:

$$[-\ln(1 - X_{\text{SnO}_2})]^{1/1.41} = k_{\text{app}} \cdot t \quad (6)$$

with $k_{\text{app}} = 1.76 \times 10^{-1} \cdot \exp[-7517.1/T] \cdot p_{\text{H}_2} \quad (\text{s}^{-1})$

4. Conclusion

A kinetic study on the reduction reaction of SnO_2 powder

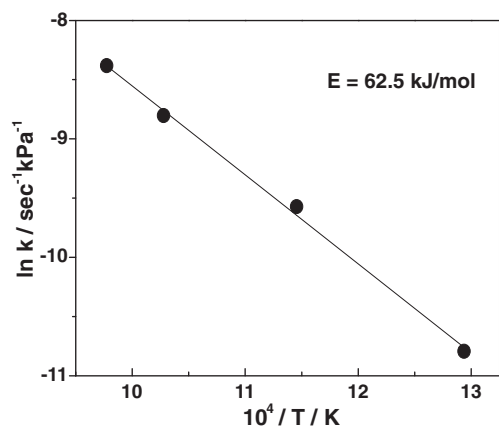


Fig. 7 Arrhenius plot of the intrinsic rate constants obtained from the results of Fig. 1.

with hydrogen gas was experimentally investigated under isothermal condition using TGA equipment. The reaction temperature was varied between 773 and 1023 K, while hydrogen partial pressures of 30.4 kPa and 101.3 kPa were done. As an example of the reaction rate, almost 100% of tin oxide was reduced to tin metal in 10 min at 1023 K under a hydrogen partial pressure of 101.3 kPa. The reduction rate was found to have an initial induction period followed by a constant and rapid period. Based on examination of the reaction rate data, the nucleation and growth model was

evaluated to be applicable in describing the kinetics of the reduction reaction of the SnO₂ powder by hydrogen. It was also calculated that the reaction was first order with respect to hydrogen partial pressure and had an activation energy of 62.5 kJ/mol (15.0 kcal/mol).

Acknowledgements

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