Modification of the Amount of CH₄ Supplied for the Efficient CH₄ Reduction of SnO₂

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Abstract: The methane reduction (MR) of SnO₂ has been proposed as a highly efficient method for recovering Sn from SnO₂ containing industrial wastes. The MR of SnO₂ also produces a mixture of H₂ and CO, which can be further utilized as a syngas for the production of various fuels through the Fisher-Tropsch process. To optimize the process parameters, we studied the effect of the amount of supplied CH₄ (CH₄/SnO₂ molar ratios of 1, 3, or 5) on the recovery of Sn from SnO₂ and the H₂/CO ratio in the produced gas. Through a combination of thermodynamic simulation and experimental confirmation, we found that the recovery rate of Sn, and the molar ratio of H₂/CO in the product gas, increased as a function of the supplied-CH₄/SnO₂ ratio. We found that the recovery of Sn increased as a function of supplied-CH₄ (95.5% at CH₄/SnO₂=5) however, the purity of Sn was consistent for all studied samples (~99.90%). Our results confirm that 3N quality high-purity Sn can be easily recovered from SnO₂ containing industrial wastes by direct solid-gas reduction.

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Keywords: SnO₂, CH₄, reduction, syngas, thermodynamic simulation, recovery rate

1. INTRODUCTION

Tin (Sn) is an essential strategic material [1-6] and is used for producing transparent electrodes (Indium-Tin Oxide: ITO) [7-11] and solder [12-14], for glass making [15-17], and the superconducting magnets in magnetic resonance imaging (MRI) instruments [18,19]. Industrial demand for Sn has gradually increased with the development of the global electronics industry, and is expected to continue to increase in the future. In nature, Sn is found as tin oxide (SnO_x), but it is also available as a recycled material. Because Sn and SnO₂ are widely used in electronic devices, solders, and glass production, recovering valuable Sn from Sn or SnO_x-containing industrial wastes is a key step in recycling Sn.

The dry reduction of SnO_x by solid carbon [20-22] is a common method of recovering Sn from SnO_x,

and utilizes cokes as a reducing agent. However, this method requires a high operating temperature and long reaction time, which inevitably leads to a limited recovery rate and poor thermal efficiency. Moreover, the process generates slag and carbon dioxide (CO₂) which require post-treatment, further reducing economic efficiency.

Another possible approach is wet smelting [23-28], which involves reducing SnO_x from Sn-plating sludge or plating liquids using chemical solutions. However, wet smelting causes significant environmental pollution because it involves corrosive liquid wastes, and is also relatively expensive.

In our previous report, we proposed a new efficient methane reduction (MR) method for SnO₂ (Eq. (3)) [29], which involved a combination of two important chemical reactions: the methane reforming reaction (Eq. (1)) [30-33] and the conventional reduction reaction using solid carbon (Eq. (2)) [20-22].

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The MR of SnO_2 utilizes the excellent reducing power of CH_4 . Because CH_4 is composed of two powerful reductants, C and H_2 , a mole of CH_4 supplies a total 3 moles of reducing agent. Interestingly, we found that instead of CO_2 , CO can be primarily produced as a gas phase product under oxygen depleted conditions with excess CH_4 . The final produced mixture of CO and H_2 can be used as a syngas and utilized for fuel production through the Fisher-Tropsch synthesis [30-33].

During the conventional reduction of SnO_x using solid carbon such as coke (Eq. (2)), CO_2 , a greenhouse gas, is also generated. Because our MR is basically free-from CO_2 production, it is a high value-added (H_2 and syngas production) and environmentally friendly (suppression of CO_2 production and utilization of CH_4 , which are both greenhouse gases) method that not only allows the recycling of valuable metals, but also produces energy sources.

In the present study, we determined the optimized amount of supplied- CH_4 (the CH_4/SnO_2 ratio, hereafter denoted R) which yields the highest Sn recovery and Sn purity. Thermodynamic simulations were initially performed to roughly study the reduction behavior at different R values. The subsequent experimental MR of SnO_2 confirmed the relationships between R and Sn recovery, Sn purity, and the H_2/CO ratio in the production gas.

2. METHODS

2.1. Thermodynamic simulation

Thermodynamic simulations were performed using the HSC chemistry 6.0 program (Outotec Research, www.hsc-chemistry.com). The equilibrium amounts of reactants and reaction products were calculated as a function of temperature. Changes in the concentration of each component in the products (reduced Sn and product gas) were predicted as a function of R ($R = 1, 3, \text{ or } 5$).

2.2. Experimental procedure

A high-purity SnO_2 electrode (98.5% SnO_2 -0.81% Sb -

Fig. 1. Schematic diagram of the experimental system for MR of SnO_2 . SnO_2 powders were placed in an alumina boat placed in the quartz tube chamber.

0.5%Cu-0.18%Fe-0.01%Pb, wt%), previously used in glass-producing electric furnaces, was acquired from Corning Precision Materials (Gumi, Korea). The SnO_2 electrode was pulverized and then sieved. The average diameter of the SnO_2 powder particles was 120 μm [29].

Figure 1 shows a schematic diagram of the reduction furnace used throughout this study. An alumina boat containing SnO_2 powder was inserted into a quartz tube chamber, which was evacuated and then heated to the target temperature (e.g., 1000 $^{\circ}\text{C}$). Before heating the chamber, the quartz tube was filled with Ar to avoid shrinkage of the quartz tube at high temperature in vacuum. To suppress the sudden temperature-drop of the chamber due to the supply of relatively cold CH_4 , and to promote the MR, the CH_4 was preheated to 185 $^{\circ}\text{C}$ by two separate heating devices before being supplied to the chamber. Once the temperature inside the tube chamber reached the target temperature, only CH_4 was supplied to initiate the MR of SnO_2 . After the MR proceeded for the desired period, the alumina boat containing the reduced SnO_2 was taken to one end of the quartz tube, outside the heating chamber. The quartz tube containing the alumina boat was cooled down to room temperature in Ar gas. Based on our previous study, the temperature and duration of the reduction reaction were set to 1000 $^{\circ}\text{C}$ and 1 h, respectively [29]. The amount of SnO_2 powder loaded in the alumina boat was 15 g per charge. To set the R value to 1, 3, or 5, the flow rate of CH_4 was set to 40.5, 121.5, or 202.5 sccm,

respectively. The product gas was collected in a plastic bag during the reaction.

The composition of the reduced Sn and the collected product gas was analyzed using inductive coupled plasma (ICP) and gas chromatography (GC-TCD). The recovery rate of Sn was estimated by the mass of reduced Sn pellets multiplied by the analyzed purity. The microstructure of the reduced Sn was analyzed using a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS).

3. RESULTS AND DISCUSSION

3.1. Thermodynamic simulation of MR of SnO_2

Figures 2(a-c) show the relative equilibrium amounts of reactants (SnO_2 , CH_4) and reaction products (Sn , SnO , H_2 , H_2O , CO , CO_2 , C) as a function of temperature. The relative amounts were calculated at

the R of 1 (a), 3 (b), and 5 (c). As the temperature increased, SnO_2 and CH_4 were decreased and Sn , H_2 , H_2O , CO , CO_2 , and C were generated. At the beginning of the MR of SnO_2 , SnO was initially formed. The amount of produced SnO increased and then decreased due to the subsequent reduction of SnO to Sn . The mechanism of the MR of SnO_2 as analyzed by density functional theory calculations in our previous study showed that the H atoms of CH_4 reduce SnO_2 first, and the remaining C atoms produce CO or CO_2 [29].

Although the temperature at which the SnO_2 is completely reduced to metallic Sn is lower than 1000°C , the relative concentration of the produced gas was stabilized at around 1000°C . In the case of $R=1$ (Fig. 2(a)), the MR of SnO_2 was completed at 625°C , and water vapor (H_2O) remained even above 1000°C . In addition, carbon was produced at the beginning of the

Fig. 2. Thermodynamic simulation of MR of SnO_2 at (a) $R=1$, (b) $R=3$, and (c) $R=5$. The R dependent concentration of the gas phase product estimated at 1000°C was calculated and presented in (d).

reaction and then decreased, and disappeared above 1000 °C.

However, for higher R values, R=3 (Fig. 2(b)) or R=5 (Fig. 2(c)), the water vapor completely disappeared, but solid carbon remained above 1000 °C. The presence of carbon at R=3 and R=5 means that the MR proceeds under oxygen depleted conditions [29]. Naturally, the C and H atoms of CH₄ reduce SnO₂. In the initial stage of the MR of SnO₂, CO₂ and H₂O are mainly produced because the reaction proceeds under oxygen rich conditions. Previously, we found that the presence of excess CH₄ promotes the gas phase reaction between CH₄, CO₂, and H₂O. The relatively stronger reductant, C, takes oxygen from H₂O. Also, CO₂ shares one of its two oxygen atoms with another C atom, producing two CO molecules. This complicated but oxygen driven gas-phase reaction vigorously occurs with R=3 and R=5, exhibiting an early depletion of H₂O and CO₂ in these conditions (Figs. 2(b) and 2(c)).

Figure 2(d) shows the trend in the concentration of CH₄, CO₂, CO, H₂, and H₂O in the product gas at 1000 °C, as a function of R. As R increases, the produced H₂O and CO₂ decreased, whereas H₂ increased. In addition, the concentration of CO increased and then decreased as R exceeded 2. As a result, at R=1, the product gas was composed of H₂, CO, CO₂, and H₂O.

On the other hand, as R reached 3 or 5, the majority of the product gas changed to H₂ and CO, which were then available to be used as syngas. Through a post-CO oxidation process, high-purity H₂ can be produced from a mixture of H₂ and CO. Moreover, a mixture of H₂ and CO can be further utilized for fuel production through the Fisher-Tropsch synthesis [29-33]. The H₂/CO ratio must be high for hydrogen production and must have an appropriate H₂ / CO molar ratio to be utilized for Fisher-Tropsch synthesis [34]. Based on our results in Fig. 2(d), we believe that the H₂/CO ratio in the produced gas can be easily controlled by adjusting R.

3.2. Experimental MR of SnO₂

Consistent with our previous findings, Figs. 2(b) and

2(c) show that all of the gas-phase products were transformed to a mixture of H₂ and CO at approximately 1000 °C. Therefore, we performed our experimental MR reduction of SnO₂ at 1000 °C. Because the experimental MR of SnO₂ was performed under continuously flowing CH₄, we allowed the SnO₂ powders to react with CH₄ for 1 hour. Ultimately, the operating temperature and reaction time should be more carefully optimized, however, we believe that this condition was sufficient to study the effect of R on the reduction behavior of SnO₂. The produced Sn was ultrasonically washed in ethanol and distilled water to remove residues.

The morphology of the SnO₂ powders and produced Sn showed that the SnO₂ powders (with a diameter range of 50 to 300 μm) were completely reduced to Sn by the CH₄ (Fig. 3). The XRD results of the composition of SnO₂ and Sn (reduced under the R=1 condition) confirmed that 1 hour of exposure to a stream of CH₄ was enough to reduce SnO₂ to metallic Sn (Fig. 4). The morphology in the X-ray diffraction (XRD) spectra showed that the acquired Sn was free of SnO₂. The XRD spectra of the reduced Sn under R=3 and R=5 showed similar results.

Figure 5(a) shows the relative concentrations of the product gases (e.g., H₂, CO, CO₂, CH₄) as a function

Fig. 3. Images of (a) SnO₂ powders used for experiments, (b) reduced Sn acquired as a result of MR of SnO₂, and (c) ultrasonicated reduced Sn pellets.

Fig. 4. XRD spectra of unreduced SnO_2 (a) and reduced SnO_2 under $R=1$ (b), $R=3$ (c), and $R=5$ (d). Figs. (b-d) show typical XRDs of pure metallic Sn.

Fig. 5. Experimentally analyzed (a) concentration of gas phase product and (b) H_2/CO ratio as a function of the R .

of R . The more CH_4 that was supplied (increasing R), the more H_2 and the less CO and CO_2 were produced, leading to an increasing H_2/CO ratio in the gas phase product (Fig. 5(b)). The appropriate H_2/CO ratio for the Fisher-Tropsch synthesis is dependent on the type of desired fuel [34]. However, mostly, $\text{H}_2/\text{CO} = 2$ is regarded an acceptable value for various fuel types, and also for prototype laboratory level experiments [34]. Our findings suggest that the H_2/CO ratio in the gas phase product can be easily controlled by R .

The overall experimentally observed trend in the H_2/CO ratio in the product gas generally followed the simulation results (Fig. 2(d)). Of course, because our thermodynamic simulations were performed under closed systems, unlike our experimental conditions, detailed aspects of the simulation and experimental results should be carefully interpreted and compared. For example, the water vapor predicted in the thermodynamic simulation results could not be experimentally detected because our GC tests were performed at room temperature. Moreover, excess CH_4

Fig. 6. ICP-analyzed composition of produced Sn pellets presented as a function of the R.

which bypassed SnO₂ without any reaction was also detected in the experimental GC results. Although the presence of unreacted CH₄ is disadvantageous for the efficient MR of SnO₂, because an almost consistent amount of bypassed CH₄ was observed for R=3 and R=5 (Fig. 5(a)), we believe that our results on the effect of R on the recovery and the purity of reduced Sn, which will be discussed below, are reasonable.

Figure 6 shows the composition of reduced Sn pellets (shown in Fig. 3(c)) as a function of R. The reduced Sn was high quality with a Sn concentration of 99.9%, containing only a small amount of Cu (< 0.09%) and Pb (< 0.006%), which could be removed by subsequent electrolytic refining. Only a marginal change was observed in the Sn purity with increasing R, meaning that the purity of the reduced Sn is determined by the intrinsic reducing power of CH₄ or by the impurity (Cu, Pb) level, rather than the amount of the reductant, CH₄. If SnO₂ meets with CH₄ in a reaction chamber, all SnO₂ can be sufficiently reduced under R=1, R=3, and R=5 as shown in Fig. 2. On the other hand, the impurities cannot be removed by CH₄ even though they meet with CH₄. So, the concentrations of Sn and impurities hardly change. On the other hand, the Sn recovery rate was slightly increased from 93.3% (R=1) to 95.5% (R=5) with increasing R (Fig. 7). The recovery of 95.5% is significantly higher than the previously reported recovery rate for the MR of SnO₂ (79.9%) in our

Fig. 7. Response of the Sn recovery rate to the R. Overall recovery greater than 93 % was achieved in all conditions.

previous study [29], indicating that the effectiveness of the MR of SnO₂ can be improved by controlling the R value. Since all SnO₂ can be reduced under R=1, R=3, and R=5, if SnO₂ can meet CH₄ with strong reducing power, the Sn recovery rate will be determined by the potential that SnO₂ and CH₄ will meet. Therefore, in this study, the increase in the Sn recovery rate with increasing R is attributed to the increase in opportunity for SnO₂ and CH₄ to meet.

A cross-sectional SEM image (Fig. 8(a)) of a reduced Sn pellet acquired after a shorter period of reduction time, 40 minutes, shows an interesting feature of the MR of SnO₂, which has its source in the low melting temperature of Sn. The interface formed between the reduced metallic Sn and the unreacted SnO₂ suggests that a portion of the pre-reduced metallic molten Sn may cover the surface of the SnO₂ powders during reduction (at 1000 °C). The formation of such a SnO₂-Sn interface would prevent direct interaction between the SnO₂ and CH₄ and result in a significant drop in the recovery rate above the melting temperature of Sn. However, we note that our laboratory-scale experiments were performed in a quartz tube furnace using an alumina boat loaded with SnO₂. This SnO₂-Sn interface formation issue can be resolved by more carefully designed reaction systems. For example, if a vertical reaction furnace is used, CH₄ can penetrate the stacked SnO₂ and reduced

Fig. 8. (a) Cross-sectional SEM micrograph of the reduced SnO₂ for 40 min at 1000 °C. The unreacted SnO₂ powders were covered by reduced Sn. When the reaction time was increased to 60 min, most of the unreacted SnO₂ powders were disappeared. (b) EDS analysis result of the reduced Sn (spectrum 1 in (a)). (c) EDS analysis result of the unreacted SnO₂ powder (spectrum 2 in (a)). (d) XRD spectrum of the reduced Sn and unreacted SnO₂ powders.

metallic molten Sn can flow down the furnace and be collected. Figs. 8(b-c) and (d) are the EDS results and XRD spectrum, respectively, of the reduced metallic Sn and unreacted SnO₂, showing that SnO₂ was being reduced to pure Sn. From our combinatorial study of thermodynamic simulations and experimental tests, we found that 3N quality high-purity Sn was recovered by the MR of SnO₂.

In this work, a high-purity SnO₂ electrode, which contained few impurities, was used as the SnO₂ source for experimental studies. More extensive studies of the MR reduction of other SnO_x sources, such as cassiterite ore, Sn-plating sludge, or flue dust, will be conducted in future works.

4. CONCLUSION

Based on our previously proposed MR of SnO₂, we further modified the process by controlling R (the CH₄/SnO₂ ratio). The effects of the amount of supplied CH₄, R, on the reduction of SnO₂ and the generation of syngas were simulated and the results were verified by experiments. A significant improvement in

the Sn recovery ratio, from 79.9% to 95.5%, was achieved by carefully controlling R. 3N quality of high purity Sn was acquired as a result of the MR of SnO₂. As R was increased, the concentration of H₂ in the production gas also increased. On the other hand, the opposite response was observed for the CO and CO₂ concentration and R. As a result, a direct proportional relationship between the H₂/CO molar ratio and R was observed, meaning that the H₂ concentration in the production gas can be intensively controlled by R. Our results present a novel method of metal recovery from corresponding metal-oxides, which could be widely applied for recycling, smelting, and refining. Moreover, our findings confirm that the key quality factors, such as the recovery ratio and the H₂ concentration in the produced gas, can be fine-tuned by controlling R, verifying the versatility of the MR method.

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