Efficient Sn Recovery from SnO₂ by Alkane (CₓHᵧ=2ₓ+2, 0 ≤ x ≤ 4) Reduction

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We study the mechanism of alkane reduction of SnO₂ for efficient low-temperature recovery of Sn from SnO₂. Based on thermodynamic simulation results, we comparatively analyze the reduction behavior and the efficiency of SnO₂ reduction by H₂ and alkanes (CₓHᵧ=2ₓ+2, 0 ≤ x ≤ 4). We found that alkanes (n-CₓHᵧ) with the higher nx generally complete the reduction of SnO₂ (T₁₀₀) at the lower temperature. Moreover, the T₁₀₀ of the SnO₂ reduction by alkanes (n-CₓHᵧ) was decreased from the T₁₀₀ of pure hydrogen with the same amount of hydrogen atoms (n-H₂). We found that the concentration of a gas phase product mixture, the amount of the produced solid carbon, and the T₁₀₀ complementary vary as a function of the nx and ny, the total amount of carbon and hydrogen atoms in the reducing gas phase molecules. Our results demonstrate a viability of the low temperature reduction method of SnO₂ by alkanes for efficient recovery of Sn from SnO₂, which can be applied for Sn recovery from Sn containing industrial wastes or Sn ores with economic value added that is held by the co-produced H₂.

Recovering (extracting) valuable metallic elements from industrial wastes is technically important for the efficient recycle of earth unabundant resources. However, the current dry-smelting, hydro-smelting, or combined smelting-electrolytic refining technologies, which are commonly applied for extraction of high purity metals from ores or used oxidized scraps, are not environmentally friendly¹–⁹. Because the high quality minable ores deplete first, designing environmentally friendly techniques are necessary to set up ecofriendly recovery processes of used metals.

Although Sn (Tin) is relatively earth unabundant among the industrially demanded metals, Sn and Sn oxides play a key role in several electronic devices and products such as sensor¹⁰,¹¹, Pb-free solder¹²,¹³, or transparent electrode¹⁴–¹⁶. Despite of the high LME (London Metal Exchange) market price ($16,450.00/metric ton as of October 4, 2019) of Sn¹⁷, which is more than 3 and 1.5 times expansive than Cu and Ni, respectively, 70% of the annually consumed Sn is not appropriately recycled¹⁸. Recovery of Sn from used SnO₂ or oxidized metal scrap proceeds in a similar process with the ore smelting in the presence of a proper and strong reducer, usually cokes. However, a poor solid-solid contact between SnOₓ and cokes and a high operation temperature lowers the overall efficiency¹⁹.

In our previous report²⁰,²¹, we have designed a methane reduction (MR) method, an ecofriendly and simple versatile process of Sn recovery from SnO₂ containing industrial wastes, which also can be potentially applied for Sn ore smelting. A direct facile contact between gas phase methane and SnO₂ improves the efficiency of the reaction. Moreover, multiple reductants provided by methane (hydrogen and carbon) sequentially reduce SnO₂, producing H₂O, H₂, CO, or CO₂ depending on the reduction conditions²¹. The geometry of a SnO₂ bound methane inhibits the initial participation of the carbon of methane to the reduction process²¹. Rather, the released hydrogen atoms from methane attribute to the initial reduction power of methane²¹. The extended release of two kinds of reducing agents from methane assures the versatility of the MR of SnO₂ and the increased economic efficiency²¹. Another interesting finding was that the H₂/CO ratio in the produced gas varies as a function of the CH₄/SnO₂ ratio. We found that the H₂/CO ratio increases if the MR of SnO₂ proceeds under oxygen depleted conditions because the late released more oxophilic carbon takes up oxygen atoms from SnO₂ and gas phase H₂O²¹.

Unique chemistry between Sn and CH₄ has reported in a recent study by the Metiu and McFarland groups²². They found that molten Sn and other transition metals can directly dissociate CH₄ into solid C and H₂ and suggested that such direct H₂ production from CH₄ without CO₂ formation as an advanced H₂ production method

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Figure 1. Theoretical prediction of the H2 reduction of SnO2. (a–c) Equilibrium concentration of the mixture of one mole of SnO2 and n-CH2 (n = 2, 4, or 6) as a function of temperature. (a) H2/SnO2 = 2, (b) H2/SnO2 = 4, and (c) H2/SnO2 = 6. The red arrows in (b) and (c) indicated the T100.

| Amount of supplied H2, n, (kmol) | 2   | 4   | 6   | 8   | 9   | 10  |
|----------------------------------|-----|-----|-----|-----|-----|-----|
| T100 (°C)                        | n/a | 615 | 545 | 494 | 484 | 464 |

Table 1. T100 of n-H2 reduction of SnO2 as a function of the amount of supplied H2, n. ‘Reduction was not completed up to 1200°C.

from hydrocarbons22. Based on our previous findings on the CH4 reduction of SnO221, we have reached to a hypothesis that use of alkanes with more carbon and hydrogen contents per mole (CxHy, 0 ≤ x ≤ 4) would accelerate the SnO2 reduction and also lower the reaction temperature. Moreover, if produced upon SnO2 reduction by alkanes, assists dissociation of alkanes into carbon and hydrogen, the SnO2 reduction would occur under the stronger reduction atmosphere so that the overall SnO2 reduction will be greatly accelerated.

In this letter, we use a combined study of thermodynamic simulations and density functional theory (DFT) calculations to study the effect of the C/H2 ratio in the reducing gas on the efficiency of the reduction of SnO2. To provide a fundamental insight into the mechanism of SnO2 reduction by alkanes with the higher carbon and hydrogen contents per mole and further clarify the reduction potential of the applied alkanes, we introduce commercially available alkanes (C10Hx+6, 2 ≤ x ≤ 4) as a reducing agent for SnO2 reduction. The efficiency of the alkane reduction of SnO2 is evaluated by the reduction complete temperature, T100, and compared with the T100 of mole-balanced pure hydrogen. We find that the T100 is an inverse exponential function of the amount of supplied reducing agent (H2 or alkane) and that the addition of carbon as a form of alkane significantly lowers the T100 from that of the H2 reduction of SnO2. Our findings predict that the operation temperature of the alkane reduction of SnO2 can be adjusted by controlling the composition and the x/y ratio of the reducing gas, suggesting an easy and industrially highly accessible recycling process of SnO2 containing industrial wastes.

Results and Discussion

H2 reduction of SnO2. Figure 1 shows the equilibrium concentrations of the mixture of SnO2 and n-H2 (n = 2, 4, or 6) at between 0 to 1200°C. Obviously, H2 reduces SnO2 into Sn through a two-step process. In all cases, SnO2 was first transferred to SnO. SnO was formed at below the melting temperature of Sn (231.9°C) and further transferred to metallic Sn upon temperature increase. Under the stoichiometric condition (H2/SnO2 = 2, 2 moles of H2 is required to reduce a mole of SnO2 to Sn and 2H2O), the reduction does not complete even at 1200°C and SnO survives. The T100 at which SnO2 and SnO were completely reduced to Sn, was significantly decreased upon increase of the amount of supplied H2 up to 4 or 6 moles (H2/SnO2 = 4 or 6, respectively, Table 1). Because consistent two moles of H2 were used for SnO2 reduction to Sn, irrespective to the initial H2/SnO2 ratio, the decrease of the T100 is presumably due to the increased chemical potential of gas phase H2 upon increase in the H2/SnO2 ratio.

Alkane reduction of SnO2: methane and ethane. Figure 2 shows the equilibrium concentrations of the mixture of SnO2 and n-CH4 (Fig. 2a,b) or n-C2H6 (Fig. 2c,d) (n = 2 or 4) at between 0 to 1200°C. Like the cases of the H2 reduction of SnO2, the T100 is equal to the point at which the SnO and SnO2 are completely depleted. Because a mole of CH4 supplies total five units of reducing agents (one C and four H), a mole of SnO2 can be easily reduced to metallic Sn. The increase of H2, C, and H2O above 200°C shows that CH4 was decomposed into C and H2 and the released H2 from CH4 initially reduces SnO2. The delayed increase of CO2 compared to the increase of CO and H2 means that C takes up oxygen from SnO2 under C and H2 rich conditions. Despite the active role of hydrogen in the early stage of the reduction, carbon completes the reduction and hydrogen of CH4 was released as gas phase H2. The T100 of CH4 reduction of SnO2 also decreases response to the increase of the CH4/SnO2 ratio (Table 2).
The overall reduction process, initial active reduction of \( \text{SnO}_2 \) by \( \text{H}_2 \) and complete reduction by \( \text{C} \), was consistently appeared in the \( \text{C}_2\text{H}_6 \) reduction of \( \text{SnO}_2 \). \( \text{C}_2\text{H}_6 \) decomposes rapidly into \( \text{C} \) and \( \text{H}_2 \) and the overall reduction occurs under highly reducible conditions. However, although the reduction occurs under \( \text{C} \) and \( \text{H}_2 \) rich conditions, \( \text{SnO} \) was also appeared as an intermediate, showing that the reduction of \( \text{SnO}_2 \) occurs through a two-step process. The rapidly increased \( \text{H}_2 \) upon \( \text{C}_2\text{H}_6 \) decomposition gradually decreased as \( \text{H}_2 \) was transformed to \( \text{H}_2\text{O} \).

Like the case of \( \text{CH}_4 \) reduction of \( \text{SnO}_2 \), \( \text{C} \) takes up oxygen, being transformed to \( \text{CO}_2 \) and eventually, to \( \text{CO} \). Most of the \( \text{H}_2 \) transformed to \( \text{H}_2\text{O} \) was released upon \( \text{CO} \) formation. When the \( \text{C}_2\text{H}_6/\text{SnO}_2 \) increases to 4, the excess \( \text{C} \) was remained as solid state carbon even after complete reduction of \( \text{SnO}_2 \). The \( T_{100} \) values of \( \text{C}_2\text{H}_6 \) reduction of \( \text{SnO}_2 \) were generally lower than the values of \( \text{CH}_4 \) reduction of \( \text{SnO}_2 \) (Table 2). The effect of the amount of \( \text{C} \) and \( \text{H}_2 \) in reducing alkanes on the \( T_{100} \) will be discussed below.

**Alkane reduction of \( \text{SnO}_2 \): propane and butane.** \( \text{C}_3\text{H}_8 \), propane, and \( \text{C}_4\text{H}_{10} \), butane, are commercially widely available alkanes and a component of liquid petroleum gas. No meaningful changes in the reduction behavior was observed in the \( \text{C}_x\text{H}_y \) reduction of \( \text{SnO}_2 \). \( \text{C}_3\text{H}_8 \) decomposes rapidly into \( \text{C} \) and \( \text{H}_2 \) and the overall reduction occurs under highly reducible conditions. However, although the reduction occurs under \( \text{C} \) and \( \text{H}_2 \) rich conditions, \( \text{SnO} \) was also appeared as an intermediate, showing that the reduction of \( \text{SnO}_2 \) occurs through a two-step process. The rapidly increased \( \text{H}_2 \) upon \( \text{C}_3\text{H}_8 \) decomposition gradually decreased as \( \text{H}_2 \) was transformed to \( \text{H}_2\text{O} \). Like the case of \( \text{CH}_4 \) reduction of \( \text{SnO}_2 \), \( \text{C} \) takes up oxygen, being transformed to \( \text{CO}_2 \) and eventually, to \( \text{CO} \). Most of the \( \text{H}_2 \) transformed to \( \text{H}_2\text{O} \) was released upon \( \text{CO} \) formation. When the \( \text{C}_x\text{H}_y/\text{SnO}_2 \) increases to 4, the excess \( \text{C} \) was remained as solid state carbon even after complete reduction of \( \text{SnO}_2 \). The \( T_{100} \) values of \( \text{C}_x\text{H}_y \) reduction of \( \text{SnO}_2 \) were generally lower than the values of \( \text{CH}_4 \) reduction of \( \text{SnO}_2 \) (Table 2). The effect of the amount of \( \text{C} \) and \( \text{H}_2 \) in reducing alkanes on the \( T_{100} \) will be discussed below.

**Modelling the reduction trend in alkanes** \( (n\cdot\text{C}_x\text{H}_y=2x+2, 0 \leq x \leq 4) \). The equilibrium concentration diagrams presented in Figs 1 and 2 show that the overall reduction process of \( \text{SnO}_2 \) by \( \text{H}_2 \) and alkanes \( (n\cdot\text{C}_x\text{H}_y\geq2x+2, 0 \leq x \leq 4) \) does not differ a lot. Vigorous release of \( \text{H}_2 \) at low temperatures from alkanes generates the similar reducing atmosphere with the reduction by pure \( \text{H}_2 \). Addition of the released \( \text{C} \) from alkanes induces the

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**Table 2.** \( T_{100} \) of \( n\cdot\text{C}_x\text{H}_y = 2x+2 \) reduction of \( \text{SnO}_2 \) as a function of the amount of supplied alkanes, \( n \).

| \( n\cdot\text{C}_x\text{H}_y \) | \( T_{100} \) (°C) |
|-----------------|-----------------|
| \( n\cdot\text{CH}_4 \) | 545 |
| \( 2\cdot\text{CH}_4 \) | 534 |
| \( n\cdot\text{C}_2\text{H}_6 \) | 444 |

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*Figure 2.* Temperature dependent evolution of equilibrium concentration of reactants and products during (a,b) \( \text{CH}_4 \) or (c,d) \( \text{C}_2\text{H}_6 \) reduction of \( \text{SnO}_2 \). (a) \( \text{CH}_4 + \text{SnO}_2 \), (b) \( 2\cdot\text{CH}_4 + \text{SnO}_2 \), (c) \( \text{C}_2\text{H}_6 + \text{SnO}_2 \), and (d) \( 2\cdot\text{C}_2\text{H}_6 + \text{SnO}_2 \).
gas phase conversion of H2O into H2. Moreover, as the alkane/SnO2 ratio increases from 1 to 2, the T100 decreases. The response of the T100 as a function of the total amount of supplied C, \( n_x \), and H, \( n_y \), is presented in Tables 2, 3 and Fig. 4a.

Considering that the T100 values are exponentially decreasing upon increase of \( n_x \) and \( n_y \) and that the addition of C affects to the T100, we presented the T100 values as a function of \( n_x \) (Fig. 4b) or \( n_y \) (Fig. 4c). Figure 4b shows that once the amount of C, \( n_x \), is given, the T100 just slightly varies upon change in \( n_y \), presenting the quite prominent and dominant effect of C on the T100 of SnO2 reduction by alkanes, as predicted by thermochemical data: the standard formation enthalpy of CO2, \( \Delta H_f^{\circ}(CO_2, 298 \, K) = -393.474 \, \text{kJ/mol} \), is greater than that of water, \( \Delta H_f^{\circ}(H_2O, 298 \, K) = -285.830 \, \text{kJ/mol} \). Because single C atom can take over two O atoms from SnO\(_2\), whereas two H atoms are required to remove one O atom from SnO\(_2\), C of alkanes will naturally more aggressively reduce SnO\(_2\).

In Fig. 4c, to more intensively compare the effect of C on the T100 of SnO\(_2\), we presented a pair of dataset, the T100 values of H2 or alkane reduction of SnO\(_2\) as a function of \( n_y \). The control group data, the T100 values acquired from H2 reduction of SnO\(_2\), gradually decrease as a function of \( n_y \): 615 °C at H2/SnO\(_2\) = 8 and 464 °C at H2/SnO\(_2\) = 20. The filled square data points in Fig. 4c represent the T100 of SnO\(_2\) reduction by \( n \cdot \text{CH}_4 \), \( n \cdot \text{C}_2\text{H}_6 \), \( n \cdot \text{C}_3\text{H}_8 \), and \( n \cdot \text{C}_4\text{H}_{10} \). For the cases where two or more combinations of alkanes are available to match the total amount of supplied hydrogen, \( n_y \), we took the case with the higher \( n_x \). For example, we took the T100 from 2C\(_2\)H\(_6\) (\( n_x = 4 \)) rather than that from 3CH\(_4\) (\( n_x = 3 \), \( n_y = 8 \)) to compare with the T100 from 6H\(_2\) (\( n_y = 12 \)). The T100 values of alkane reduction of SnO\(_2\), fitted to an exponential function, show a significantly decrease in T100 (Fig. 4c). Replacing a reducing agent from 4 moles of H\(_2\) (\( n_y = 8 \)) to a mole of C\(_3\)H\(_8\) (\( n_x = 3 \), \( n_y = 8 \)) decreased the T100 of a mole of SnO\(_2\) from 615 °C to 494 °C (Fig. 4c). The fitted exponential curves of T100 as a function of \( n_x \) or \( n_y \) (solid lines in Fig. 4b,c) show that the T100 of the alkane or H2 reduction can be fit to simple exponential functions (refer to Tables 4 and 5 for fitting constants and R\(^2\)-values).

Interestingly, we found that the \( \Delta T_{100} \) (T\(_{100}\)-alkane – T\(_{100}\)-hydrogen), an indicator of the effect of carbons from alkanes on the reduction of SnO\(_2\), was \(-121 \, \text{°C} \) at \( n_y = 3 \) and rapidly saturated to \(-101 \, \text{°C} \) at \( n_y = 4 \) and beyond (Fig. 4c). The \( \Delta T_{100} \) calculated from the two fitted exponential curves predicts the slightly fluctuating \( \Delta T_{100} \)
centered at −105 °C (Fig. 4d). Because the \( \Delta T_{100} \) was estimated comparing the (0, \( ny \)) and (\( nx \), \( ny \)) data points with the maximum \( nx \) value, it naturally represents the maximum effect of C addition to the \( T_{100} \) reduction. The overall increase of \( nx \) and \( ny \) is beneficial for \( SnO_2 \) reduction because the lower \( T_{100} \) assures the higher economic efficiency. However, the effect of additional C to the \( T_{100} \) is limited to \( \Delta T_{100} \approx -105 °C \). The vertically separated three data points in Fig. 4c, (0, 8), (2, 8), and (3, 8), show that the effect of C on the \( T_{100} \) increase as a function of C addition. Because C released from alkanes aggressively attack H\(_2\)O and liberate hydrogens of H\(_2\)O\(_2\), the presence of excess C may increase the chemical potential and the reducing potential of gas phase H\(_2\).

**Figure 4.** Effect of C on the \( T_{100} \) of H\(_2\) or alkane reduction of SnO\(_2\). (a) A 3-dimensional diagram of \( T_{100} \) of alkane reduction of SnO\(_2\) presented as a function of \( nx \) and \( ny \). (b) \( T_{100} \) values of alkane reduction of SnO\(_2\) plotted as a function of \( nx \). The pairs of numbers in the parentheses present the total units of C, \( nx \), and H, \( ny \), in alkanes. (c) \( T_{100} \) values of H\(_2\) or alkane reduction of SnO\(_2\) plotted as a function of \( ny \). The pairs of numbers in the parentheses present the total units of C, \( nx \), and H, \( ny \), in reductants. Red and green lines present the fitted exponential functions of \( T_{100} \) as a function of \( ny \). (d) \( \Delta T_{100} \) values estimated from the two fitted exponential curves of \( T_{100} \).

Reference function \( T_{100} = \exp [a + b (nx) + c(nx)^2] \), \( 1 \leq nx \leq 10 \)

| \( C_nH_m \) reduction of SnO\(_2\) \ | \( a \) | \( b \) | \( c \) | Adjusted R\(^2\) |
|---|---|---|---|---|
| 6.5413 | -0.1340 | 0.0067 | 0.9898 |

**Table 4.** \( T_{100} \) of alkane reduction of SnO\(_2\) fitted to an exponential function of \( nx \).

Reference function \( T_{100} = \exp [a + b (ny) + c(ny)^2] \), \( 0 \leq ny \leq 20 \)

| \( H_2 \) reduction of SnO\(_2\) \ | \( a \) | \( b \) | \( c \) | Adjusted R\(^2\) |
|---|---|---|---|---|
| 6.7477 | -0.0479 | 8.8363 \times 10^{-4} | 0.9956 |
| \( C_nH_m \) reduction of SnO\(_2\) \ | \( a \) | \( b \) | \( c \) | Adjusted R\(^2\) |
| 6.6350 | -0.0629 | 0.0013 | 0.9834 |

**Table 5.** The \( T_{100} \) of H\(_2\) or alkane reduction of SnO\(_2\) fitted to an exponential function of \( ny \).

centered at −105 °C (Fig. 4d). Because the \( \Delta T_{100} \) was estimated comparing the (0, \( ny \)) and (\( nx \), \( ny \)) data points with the maximum \( nx \) value, it naturally represents the maximum effect of C addition to the \( T_{100} \) of SnO\(_2\) reduction. The overall increase of \( nx \) and \( ny \) is beneficial for SnO\(_2\) reduction because the lower \( T_{100} \) assures the higher economic efficiency. However, the effect of additional C to the \( T_{100} \) is limited to \( \Delta T_{100} \approx -105 °C \). The vertically separated three data points in Fig. 4c, (0, 8), (2, 8), and (3, 8), show that the effect of C on the \( T_{100} \) increase as a function of C addition. Because C released from alkanes aggressively attack H\(_2\)O and liberate hydrogens of H\(_2\)O\(_2\), the presence of excess C may increase the chemical potential and the reducing potential of gas phase H\(_2\).

**Reaction mechanism of alkane reduction of SnO\(_2\).** As a prototypical example of alkane reduction of SnO\(_2\), DFT-calculated reaction mechanism of CH\(_4\) reduction of SnO\(_2\) is presented in Fig. 5a. The original DFT-calculated reaction energy values were adopted from our previous publication (Under Creative Commons
The initial CH₄ dissociative adsorption (Process #1, Fig. 5a) initiates the CH₄ reduction of SnO₂. Because a CH₄ molecule was dissociated into a –CH₃ methyl group and a hydrogen atom, which are independently bound to surface lattice oxygen atoms of SnO₂, the SnO₂ surface will be strongly hydrogenated upon exposure to CH₄. The sequential combined processes of dehydrogenation of –CH₃ to –CH (Processes #2 to #5) and water formation (process #3 and #4) are energetically uphill. This is because two hydrogen atoms produced upon dehydrogenation of a single CH₄ molecule were used for water formation. As we discussed above, under the CH₄ rich reduction conditions, the surface oxygen ions of SnO₂ will be eventually hydrogenated and thus the endothermic dehydrogenation of –CH₃ and water formation will not hinder the overall reduction of SnO₂. The second water formation (Process #6 and #7) and CO₂ production (Process #8) are energetically downhill.
strongly thermodynamically preferred. The overall reduction of SnO₂ by CH₄ shows that the hydrogen atoms of CH₄ participate in the reduction process first and the residual carbon atom finally reduces SnO₂. This finding is consistent with the equilibrium concentration diagrams (Figs 2 and 3) showing that H₂O always forms first to CO and CO₂. 

Interestingly, upon initial adsorption of C₃H₈ and C₄H₁₀, multiple –OH and –CH₃ groups were formed as a result of dissociative adsorption of alkanes (Fig. 5b–d). Later, each –CH₃ group was eventually dissociated into –CH₂ and –OH, therefore the subsequent –CH₂ dissociation, water formation, and CO₂ formation processes would saturate into the same processes presented in Fig. 5a. The overall reaction mechanism of SnO₂ reduction by alkanes (C₃H₈₋₂≤x≤₄, 0 ≤ x ≤ 4), therefore, is identical to each other except for the detailed energetics of the initial dissociative binding step. Interestingly, the initial dissociative adsorption of C₃H₈ and C₄H₁₀ are energetically endotherm (Fig. 5c,d). However, considering that the alkane reduction would occur under the high alkane partial pressure conditions⁹,¹³, the highly negative entropic contribution to the Gibbs free energy of binding, –TΔS, will definitely compensate the positive ΔE of dissociative adsorption (ΔE in Fig. 5c,d)⁹,¹³, making the ΔG of dissociative C₃H₈ and C₄H₁₀ binding negative (exothermic). The roughly calculated highly negative –TΔS at standard state⁹ of propane (−0.83 eV) and butane (−0.95 eV) confirm that the ΔG values of dissociative alkane bindings (ΔG = ΔE − TΔS) are negative. The DFT-calculated mechanism of alkane (C₃H₈₋₂≤x≤₄, 0 ≤ x ≤ 4) reduction of SnO₂ shows that the overall reaction mechanism is consistent within the alkane that we applied (C₃H₈₋₂≤x≤₄, 0 ≤ x ≤ 4) for SnO₂ reduction, irrespective to x and y. This result confirms that the significantly accelerated reduction potential of alkanes upon increase in nx is due to the quantitatively excessive supply of reducing agents by alkanes with the higher nx. As we have noticed in the introducing part, the presence of the already reduced liquid Sn metal may assist the direct reduction of alkanes. If this process occurs, the overall reaction will proceed under the conditions (under the total pressure greater than 1 atm) with excessive solid state carbon supply. Results on the mechanism of SnO₂ reduction by alkanes under the various conditions (partial pressure and carbon content) will be reported in due course.

**Conclusions**

We study the mechanism of alkane reduction of SnO₂ for efficient low-temperature recovery of Sn from SnO₂ using combined study of thermodynamic simulations and DFT calculations. Through a comparative analysis of the reducing power of H₂ and commercially available alkanes (CₓHₓ₋₂≤x≤₄, 0 ≤ x ≤ 4) toward SnO₂ reduction, we scaled the reducing potential of studied reductants with T₁₀₀, the temperature at which SnO₂ is completely converted to metallic Sn. The alkanes with the higher nx and ny quickly complete the reduction at low T₁₀₀. Moreover, the positive effect of nx on the T₁₀₀ was quite prominent in all studied cases of alkane reduction of SnO₂. The T₁₀₀ of the SnO₂ reduction by alkanes (n-CₓHₓ) was significantly decreased from the T₁₀₀ of pure hydrogen with the same amount of hydrogen atoms (n-H₂). The fitted exponential curves of T₁₀₀ plotted as a function of ny presents that the effect of C on the T₁₀₀ being saturated at ΔT₁₀₀ ≈ −105°C. The C and H atoms released from alkanes sequentially reduce SnO₂ to Sn and eventually to metallic Sn. The initial stage of SnO₂ reduction by alkane is identical to the H₂ reduction of SnO₂; H₂ takes up oxygen from SnO₂. However, in the presence of the released C from alkanes, H₂ of H₂O is released as a gas phase molecule as C takes up oxygen from H₂O. Because the gas phase redistribution between H₂O, H₂, CO, and CO₂, caused by solid C occurs at above the T₁₀₀, the role of the solid C released from alkanes is likely to adjust the chemical potential of hydrogen of H₂O and H₂, accelerating the reduction of SnO₂ by H₂. The DFT-calculated atomic scale mechanism of alkane reduction of SnO₂ confirmed that the overall reaction mechanism is consistent within applied alkanes (CₓHₓ₋₂≤x≤₄, 0 ≤ x ≤ 4).

Our results show that the alkane reduction of SnO₂ is an effective recovery method of metallic Sn from SnO₂ or SnO containing industrial wastes or from Sn ores. The low T₁₀₀ values of alkane reduction and the maximum ΔT₁₀₀ of −105°C suggest that the alkane reduction of SnO₂ assures high economically efficiency with economic value added that is held by the co-produced H₂ and carbons.

**Methods**

**Thermodynamic simulation.** Thermodynamic simulations were performed with the HSC 6.0 code (Outotec Research, www.hsc-chemistry.com). The relative thermodynamic stability of various Sn, C, O, and H containing chemical compounds was estimated at temperatures between 0°C and 1,200°C. The initial equilibrium simulations were performed with 1 kmol of SnO₂ balanced with increasing amount of H₂ or alkanes. The T₁₀₀ of several commercially accessible alkanes (CₓHₓ₋₂≤x≤₄, 0 ≤ x ≤ 4), methane (CH₄), ethane (C₂H₆), propane (C₃H₈), and butane (C₄H₁₀), were measured and compared with that of pure H₂ to estimate the effect of carbon addition on the reducing power of a gas phase reductant. To generalize the effect of carbon, the measured T₁₀₀ values were fitted to exponential curves.

**Density functional theory calculation.** We performed density functional theory calculations with the Vienna ab-initio simulation package (VASP)²⁷ with the Perdew-Burke-Ernzerhof (PBE)²⁸ exchange-correlation functional to study the reaction pathway and the corresponding energetics of alkane (CₓHₓ₋₂≤x≤₄, 0 ≤ x ≤ 4) reduction of SnO₂. The most bottom SnO₂ triple layer was fixed during the optimization to ensure the structural robustness of the slab models. The interaction between the ionic cores and the valence electrons was described with the projector augmented-wave method²⁹. The valence-electron wave functions were expanded in the plane-wave basis set up to the energy cutoff of 400 eV. The convergence criteria for the electronic structure and the atomic geometry were 10⁻⁶ eV and 0.03 eV/Å, respectively. The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.
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Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2017R1A2B4009829 and 2017R1A4A1015360). This work was conducted under the framework of the research and development program of the Korea Institute of Energy Research (B92441). This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, and the Scientific Data and Computing Center, a component of the Computational Science Initiative, at Brookhaven National Laboratory under Contract No. DE-SC0012704. Computing time was also provided by the National Institute of Supercomputing and Network/Korea Institute of Science and Technology Information (KSC-2018-CRE-0078).

Author contributions

H.Y.K. designed this work. M.Y., H.A. and H.H. performed thermodynamic simulations and density functional theory calculations. H.C. and E.K. analyzed the results. H.Y.K. wrote the manuscript. All the authors contributed to discuss on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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