

Study of crystal growth and kinetic parameters of Zn/ZnO oxidation in the presence of H₂O and CO₂

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Abstract During the H₂O/CO₂ co-splitting, ZnO crystals were formed by oxidation of Zn giving gaseous product, H₂/CO. Micrographs of Zn/ZnO and temperature program reaction (TPRx) of H₂O/CO₂ splitting showed that the crystal growth was occurred via two phenomena; (1) surface reaction: at temperature from 400 to 550 °C, H₂O/CO₂ oxidized Zn resulting in the outward growth of the ZnO crystals until the whole surface became inert and totally covered all the unreacted Zn inside the core. At this point, the production rates of H₂/CO were temporarily paused; (2) phase changing and core-cracking/shrinking: at temperature 550–600 °C, Zn particles inside the core was phase-changed from solid to liquid/vapor due to the higher temperature. The higher pressure inside the core led to core-cracking, where the Zn travelled to the surface to continue reacting with H₂O/CO₂. Core-shrinking was then occurred due to the crack of ZnO shell and leakage of Zn. TPRx results showed that CO₂ competed H₂O in adsorption/dissociation on the Zn during temperature from 400 to 550 °C. Conversions and kinetic parameters were experimental and mathematical determined. The apparent activation energy of H₂O and CO₂ splitting on Zn/ZnO particles was estimated at 77.63 and 51.11 kJ/mol, while the pre-exponential factors were determined at 4.02 and 0.30 s⁻¹, respectively.

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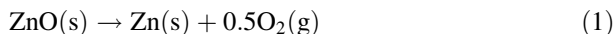
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Keywords Crystal growth mechanism · Thermochemical cycles · Zn/ZnO · H₂O/CO₂ co-splitting · Syngas production

Introduction

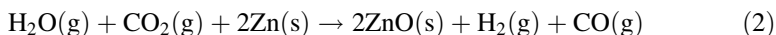
Increasing carbon dioxide (CO₂) emissions are believed to contribute to the rise in global temperature and climate changes in the phenomena coined the greenhouse effect. Nevertheless, this compound has been recently considered as an important carbon source for converting to fuels (e.g. reduction to methane) and feedstock for chemical synthesis (such as ammonia production, beverage carbonation). One valorizing example of CO₂ utilization is synthesis gas (syngas, a mixture of hydrogen and carbon monoxide) production via dissociation of H₂O and CO₂ on solid metal oxides. Syngas can be used to produce multiple value added chemicals and fuels such as Fisher-Tropsch liquids, methanol and derivatives or olefins. Conversion of H₂O and CO₂ to syngas can be performed by several methods such as direct thermolysis, electrolysis cell, photocatalysis and thermochemical cycles [1–6]. The direct thermal decomposition of H₂O and CO₂ requires ultra-high temperatures (> 2200 °C) with complicated separation unit to avoid recombination of the gaseous products, which could otherwise lead to explosion [7]. The solar-thermochemical cycles and electrolysis had been compared and it was found that electrolysis can be competitive with the solar-thermochemical process only if (1) the cost of electricity is low; (2) stability and lifetime of the electrolyzer are improved [8]. The cost of solar thermochemical cycles of metal oxides are dominated by capital costs of solar array. Development of non-expensive materials can be used in large scale production. The photocatalysis/artificial leaf directly uses solar photon energy for photochemical process while the solar-thermochemical cycles offer intriguing thermodynamic advantages with direct economic implications [9]. Several metal oxides have been investigated as oxygen carriers for thermochemical processes in the literature [10, 11]. The solar thermolysis of the ZnO system occurs at 1500–1700 °C [10] while that of the Fe₃O₄ is strongly endothermic and occurs at 2200 °C [11]. The Zn/ZnO system requires a sophisticated reactor design and a quenching system due to its phase change at 907 °C. Ceria based materials, such as pure ceria or ceria/zirconia, is a promising non-stoichiometric material since it possesses high oxygen storage capacity, created by intrinsic/extrinsic surface electronic defects, resulting in high oxygen vacancy/oxygen storage capacity. This type of material is able to take up/release oxygen without changing its structure [12]. In this work, Zn/ZnO system was selected as the oxygen carrier due to its promising high yield of the syngas compared to non-stoichiometric material such as CeO₂ and perovskites which were believed to have lower operating temperature but less product yield [13–16]. The chemical reaction of both endothermic reduction step and exothermic oxidation step of the material are presented by the following equations [13, 14]:

Endothermic thermal dissociation:



$$\Delta H_{298.15\text{ K}} = +350.5\text{ kJ mol}^{-1}$$

Exothermic H_2O and CO_2 co-splitting:



$$-108.8\text{ kJ mol}^{-1} < \Delta H_{298.15\text{ K}} < -64.7\text{ kJ mol}^{-1}$$

In Reaction 1, ZnO is thermally dissociated at high temperature (1500–1700 °C), to produce the active Zn. In Reaction (2), Zn is oxidized by water and carbon dioxide yielding high purity synthesis gas and the initial ZnO species. The exothermic second step occurs at lower temperatures (400–600 °C) and the initial ZnO species is recycled for regeneration in the Reaction 1.

The catalytic performance of Zn/ZnO towards the $\text{H}_2\text{O}/\text{CO}_2$ co-splitting was studied in a lab-scaled packed-bed reactor, from which the gaseous product was analyzed on-line using mass spectrometry at different temperature varied from 400, 450, 500, 550 and 600 °C. The conversion of the Zn to ZnO were presented at the studied temperatures and reported together with the crystal growth mechanism.

Experimental

Catalyst preparation

An aqueous solution of zinc ion reagent, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.0%, Ajax), and capping surfactant, cetyltrimethyl ammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{BrN}$, 99.0%, Fluka) were mixed and vigorously stirred until a clear and homogeneous solution was achieved. The pH of the solution was controlled by adding Hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$, 99.0%, Ajax) dropwise. The solution was stirred continuously at 70 °C for 2 h until a white suspension was formed. The white precipitate was separated by filtration of the suspension, rinsed with ethanol and water to eliminate the ionic residues and air-dried at 110 °C for 4 h. The resultant, solid material was calcined at 700 °C for 2 h in air to obtain a yellowish-white zinc oxide.

Catalyst characterization

X-ray diffraction analysis (XRD, Rigaku TTRAX III) was carried out using Cu K_α radiation with $\lambda = 1.5418\text{ \AA}$, in the range of $30^\circ < 2\theta < 80^\circ$, with 0.01° step size and scan time of $2^\circ/\text{min}$. The average crystallite size was calculated using a modified Scherrer equation [15]. The morphology of the material was examined using a field emission scanning electron microscopy technique, (FE-SEM, JSM-7001F, JEOL), operated at 15 kV. The temperature was linearly raised at a rate $10\text{ }^\circ\text{C}/\text{min}$ to 950 °C. Both XRD and SEM analysis were carried out pre- and post-reaction.

Catalytic performance test

The catalyst performance towards thermochemical cycles of H_2O and CO_2 co-splitting was evaluated in a packed bed reactor at atmospheric pressure. The reactor was a quartz tube with an internal diameter (i.d.) of 4.0 mm, positioned vertically in a tubular furnace. 30 mg of Zn was mixed with 70 mg of ZnO particles (particle size 200–400 μm , was added as an inert to slow down the reaction's kinetics and to create a better heat transfer of the overall bed). A mixed reactant gases of 5% CO_2 and 5% H_2O balanced with Ar at total flow rate of 100 mL/min was fed by Brooks flow controllers to the reactor. Weight hourly space velocity (WHSV) was maintained at 60 $\text{L g}^{-1} \text{h}^{-1}$ at room temperature (25 $^\circ\text{C}$) and atmospheric pressure (1 atm). The catalyst material was placed on a thin layer of quartz wool, used as a bed base, in the center of the tube adjacent to an electrical tube furnace. The steam generator was improvised from a set of evaporator and condenser. The partial pressure of the steam in the system was calculated using the Antoine equation. The experiment was run under isothermal conditions at 400, 450, 500, 550 and 600 $^\circ\text{C}$. The gaseous product stream was analysed online using a quadrupole mass spectrometer (MS, Omnistar GSD 320: sampling rate = 1 s^{-1} , faraday MID limit: 20 ppm) connected to the thermo-analyzer by a trace heat capillary tube (ca. 150 $^\circ\text{C}$).

The total chemical solid conversion as a function of time, $X(t)$, can be expressed as the ratio of the amounts of H_2 and CO produced at any time (t) to the initial amount of Zn in the sample:

$$X(t) = \frac{n_0 \text{ reacted}}{n_0 \text{ available}} = \frac{n_{\text{ZnO}}(t)}{n_{\text{Zn, in}}} = \frac{\int_0^{t_f} (\dot{n}_{\text{H}_2} + \dot{n}_{\text{CO}}) dt}{(m_{\text{Zn}}/M_{\text{Zn}})} \quad (3)$$

Here m_{Zn} is the initial sample mass of Zn, M_{Zn} is the molecular weight of Zn in the sample, and t_f is the reaction time. Cumulative amounts of H_2 and CO produced were calculated by integrating the production rate profiles.

$$\dot{n}_{\text{H}_2}(t) = y_{\text{H}_2}(t) \cdot v_0 \quad (4)$$

$$\dot{n}_{\text{CO}}(t) = y_{\text{CO}}(t) \cdot v_0 \quad (5)$$

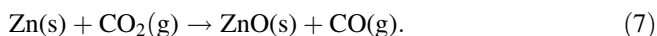
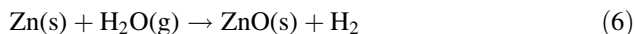
Transient temperature program reactions (TPRx) were also carried out, to investigate mechanisms of H_2O and CO_2 splitting separately. H_2O and CO_2 volumetric flow rates were set at 0.07 and 80 ml/min, respectively. The carrier gas was Ar and the total flow rate was 100 ml/min. The temperature was increased from room temperature to 700 $^\circ\text{C}$ with 5 $^\circ\text{C}/\text{min}$ heating rate.

Mathematical model

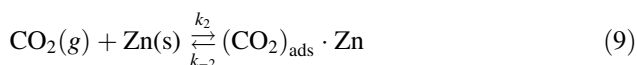
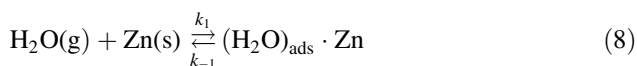
The Boltzmann equation was applied and described below [16]. The reaction kinetics in this work was proposed based on the following hypotheses: (1) the system is isothermal (2) the net reactions are irreversible (3) no external mass transfer limitation in bulk stream (4) equimolar counter-diffusion was assumed (5)

the pseudo-steady-state approximation is applicable (6) the rate is surface reaction controlled (7) amount of the solid reactant (Zn/ZnO) was small compared to H₂O and CO₂, therefore, (8) reaction order was assumed zero.

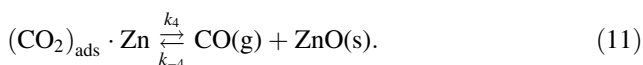
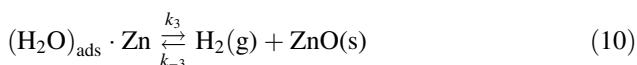
The gas–solid surface reactions of H₂O/CO₂ reacting with Zn/ZnO were predicted as:



Adsorption of H₂O/CO₂ molecules on the active sites of the Zn particle, see in Reactions 8 and 9.



Dissociation/desorption of the adsorbed H₂O/CO₂ on Zn particle are described as;



The gaseous products were continuously removed from the system, therefore, all reversible reactions were assumed negligible. The adsorption steps, which include Reactions 8 and 9, were assumed the rate controlling step [17].

$$r_1 = k_1 \theta_{\text{H}_2\text{O}} \theta_{\text{Zn}} \quad (12)$$

$$r_2 = k_2 \theta_{\text{CO}_2} \theta_{\text{Zn}}. \quad (13)$$

Let N₁ stands for mole number of the reacted Zn, N₂ for mole number of the unreacted Zn, and N for total mole number of Zn on the active sites, therefore:

$$N_1 + N_2 = N \quad (14)$$

The amount of reacted H₂O/CO₂ is proportional to the amount of the reacted Zn or the mole number of the created ZnO, where C is proposed as the proportionality coefficient which is a constant value. Hence:

$$\theta_{\text{H}_2\text{O/CO}_2} = \frac{\text{CN}_1}{N} \quad (15)$$

$$\theta_{Zn} = \frac{N_2}{N} \quad (16)$$

Let n represents amount of substance for Zn, X is the conversion of Zn, and X_u is the ultimate conversion of Zn in the rapid reaction regime, then the conversion X and X_u can be expressed as follows:

$$X = \frac{N_1}{n} \quad (17)$$

$$X_u = \frac{N}{n} \quad (18)$$

Substituting Eqs. 14–18 in Eqs. 12 and 13, we can express the rate as shown in Eq. 19:

$$r = kC \times \frac{X}{X_u} \left(1 - \frac{X}{X_u} \right) \quad (19)$$

The general reaction rate can also be expressed as Eq. 20:

$$r = \frac{dN_1}{dt} \quad (20)$$

Introducing Eq. 17 into Eq. 20, we obtain Eq. 21:

$$r = n \frac{dX}{dt} \quad (21)$$

The reaction rate then becomes:

$$r = \frac{dX}{dt} = k' \frac{X}{X_u} \left(1 - \frac{X}{X_u} \right) \quad , \quad k' = \frac{kC}{n} \quad (22)$$

$$\frac{dr}{dt} = \frac{d^2X}{dt^2} = \frac{k'}{X_u^2} \left(1 - \frac{X}{X_u} \right) \frac{dX}{dt} \quad (23)$$

At $r_{\max}$, $dr/dt = d^2X/dt^2 = 0$, then X_1 is the interest conversion giving $X_1 = X_u/2$. The Boltzmann equation below was achieved.

$$X = X_u - \frac{X_u}{1 + \exp \left[\frac{(t-t_0)k'}{X_u} \right]} \quad (24)$$

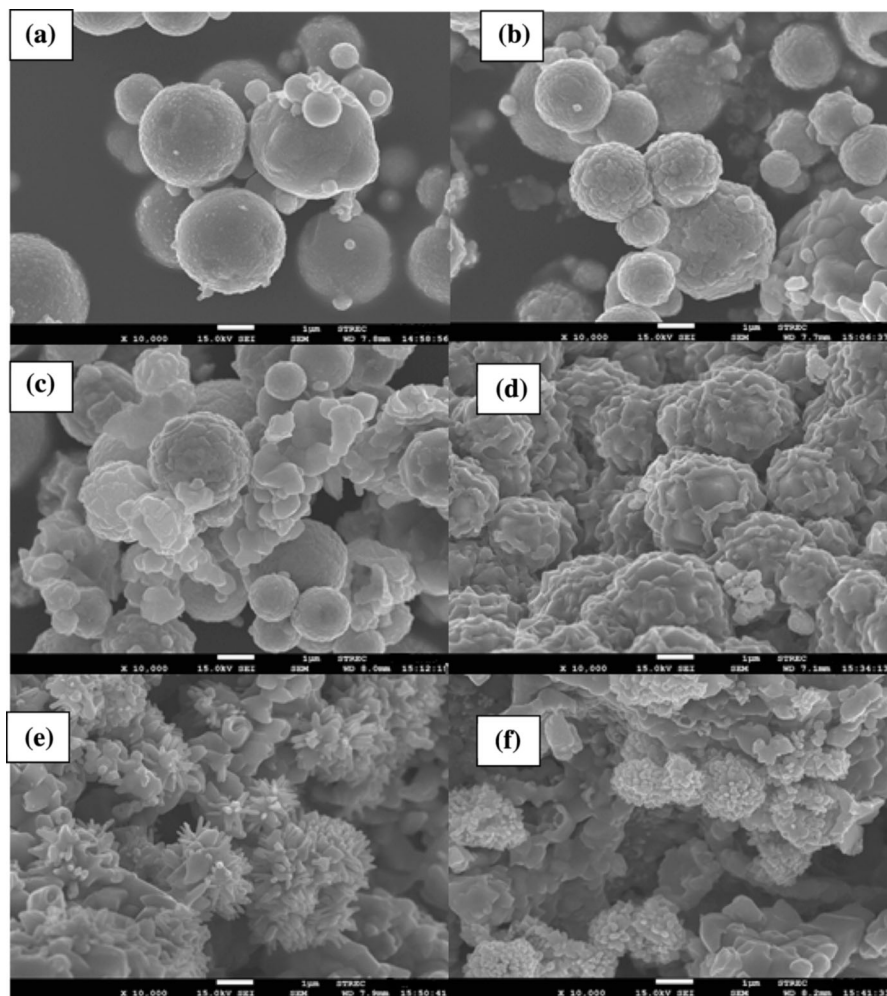


Fig. 1 SEM micrographs of **a** pre-exposure Zn/ZnO **b–f** Zn/ZnO products collected after reaction varied temperature at 400, 450, 500, 550 and 600 °C

Results and discussion

Mechanism of ZnO formation

Fig. 1 shows SEM micrographs of pre-exposure Zn (a) and post-exposure of Zn under different temperatures at 400 °C (b), 450 °C (c), 500 °C (d), 550 °C (e) and 600 °C (f).

At 400 °C, ZnO crystals started to grow and became more obvious with increasing temperature. The whole surface became rod-like with no smooth surface detected at 550 °C. At 600 °C, the particles appeared misshaped and slightly

smaller than its initial size. The detailed phenomena of the crystal growth was explained in later section.

Fig. 2 shows diffractograms of the (a) fresh Zn, (b) fresh Zn in ZnO (used as inert) (c) post-exposure Zn/ZnO at 600 °C and, (d) fresh ZnO. The fresh Zn in ZnO (b) showed ZnO as a major crystalline phase [compared with (d)] and Zn as a minor crystalline phase [compared with (a)]. After the reaction was completed at 600 °C, Zn in the Zn/ZnO mixture had been converted fully to ZnO, showing only ZnO as single crystalline phase (c), which was similar to the fresh ZnO (d).

Fig. 3 shows transient experimental results on TPRx of H₂O and CO₂ splitting, carried out separately. The reaction was considered to occur in 2 different mechanistic zones which were: zone I–surface reaction, occurring at temperature lower than 550 °C, and zone II–core shrinking/cracking, occurring at temperature higher than 550 °C. In zone I, CO₂ competed H₂O on adsorption/dissociation on the surface of the Zn resulting in higher production of CO compared to H₂ at lower temperature. When the Zn at the surface was all converted to ZnO, it then became inert so that the reaction rates of H₂O and CO₂ splitting were temporally slowed down at 550 °C. The thickness of the ZnO in CO₂ splitting was thicker than that in H₂O splitting reaction [see the illustrated diagram in Fig. 4 (area A1 and B1)]. SEM results correspondingly showed that the ZnO crystals were formed at temperature from 400 to 500 °C and grew bigger with increasing temperature (shown in Fig. 1b–d). In zone II, at temperature from 550 °C and higher, productivity of both H₂ and CO continued (see Fig. 3, areas A2 and B). This happened via 2 main phenomena; (1) phase changing of Zn and core-cracking; at this stage, the Zn was in liquid–vapor phase due to the higher temperature and pressure inside the core, causing

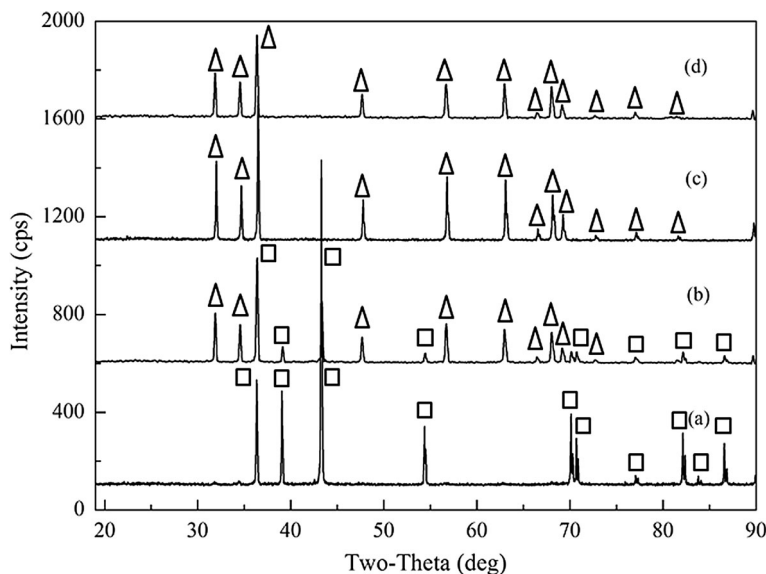


Fig. 2 XRD patterns of pre- and post-exposure Zn/ZnO **a** fresh Zn **b** fresh Zn mixed with fresh ZnO (used as inert) **c** fully reacted Zn in ZnO at 600 °C and **d** fresh ZnO

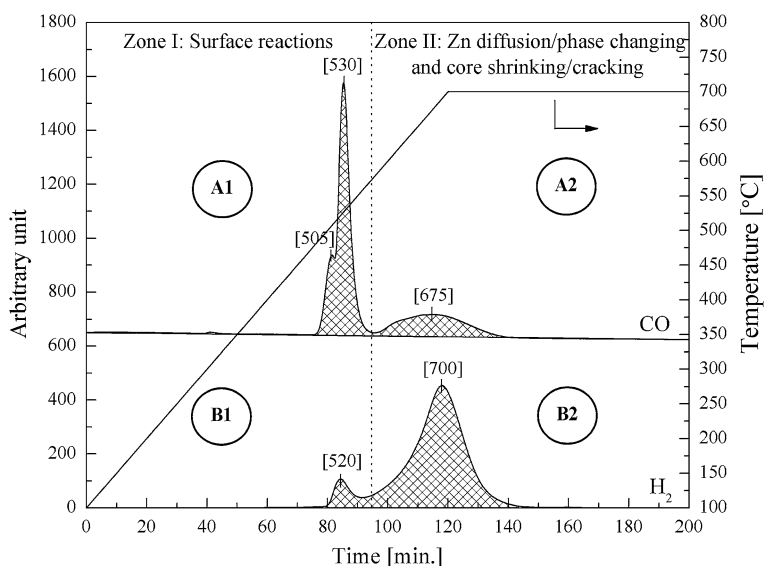


Fig. 3 Temperature programmed reaction (TPRx) of H_2O and CO_2 splitting from room temperature to 700 at $5^\circ\text{C}/\text{min}$ heating rate. Area A1, A2, B1 and B2 represented CO_2 splitting and H_2O splitting in zone 1 and zone 2

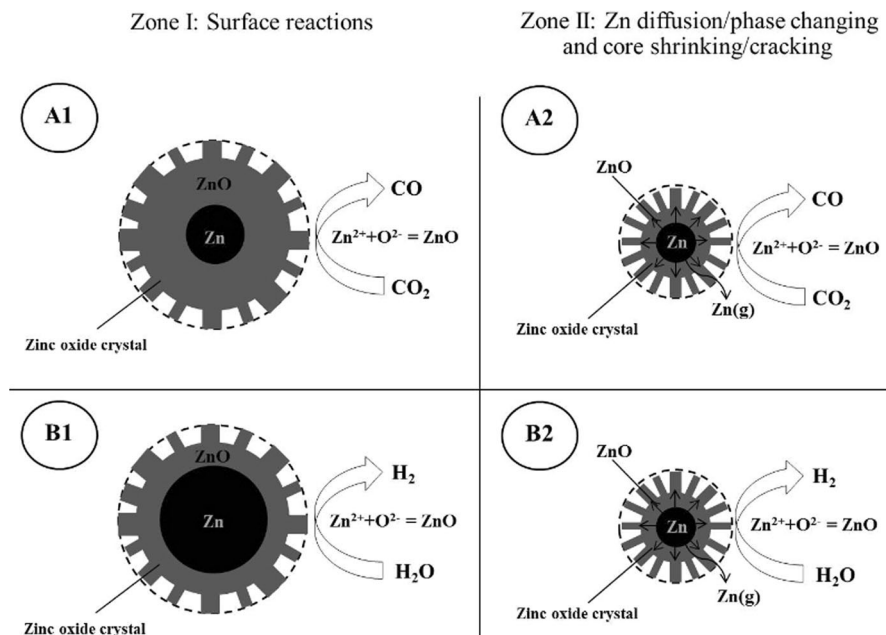


Fig. 4 Illustration of ZnO Crystal growth mechanism of oxidation of Zn in the presence of H_2O and CO_2 . (A1) CO_2 splitting on Zn at temperature below 550°C , (A2) CO_2 splitting on Zn at temperature higher than 550°C , (B1) H_2O splitting on Zn at temperature below 550°C and, (B2) H_2O splitting on Zn at temperature higher 550°C

core-cracking and shrinking. The particles then became smaller (see Fig. 1e, f). (2) Zn ions diffused through the cracks of ZnO layer to the surface and reacted further with H_2O and CO_2 showing the more obvious rod-like ZnO crystals (see Fig. 1e, f). Crystal growth mechanism was illustrated in Fig. 4, in relation to each area A1, A2, B1, B2 defined in Fig. 3.

In Fig. 4, H_2O and CO_2 reacted with Zn giving H_2 and CO while Zn was oxidized and converted to ZnO (see area B1 and A1). TPRx profiles in Fig. 3 suggested that the thickness of ZnO in A1 must be thicker than that in B1 due to the higher productivity of CO compared to H_2 in zone 1. When Zn particles at the surface were all reacted and became inert ZnO crystals, totally covered the active Zn inside the core, the drop of the productivity rates at around 550 °C was detected as shown in TPRx profiles in Fig. 3. At temperatures higher than 550 °C, the Zn inside the core started to melt/vaporize becoming liquid-vapor Zn. The pressured increased inside the core caused core-cracking which allowed Zn to diffuse to the surface and react further, at the same time, the core started to shrink due to the Zn diffusion to outside the core. This phenomenon resulted in more obvious rod-shaped ZnO at the surface while the particle size became smaller and misshaped compared to its initial form (see also Fig. 1e, f).

Experimental and modelled conversions

The experimental H_2O and CO_2 conversion to H_2 and CO were calculated from Zn to ZnO solid conversion and mole fractions of the products using Eqs. 3–5, presented in Fig. 5a and b. The reaction rate rapidly increased at the beginning when $\text{H}_2\text{O}/\text{CO}_2$ was first introduced fast chemical (reaction-controlled regime or surface reaction), and then slowly decreased until approaching constant conversions (diffusion-controlled regime or core-cracking/shrinking). The mathematical conversions were modelled using the Boltzmann equation (Reaction 24). Both mathematical and experimental conversions are in good agreement.

The kinetic parameters were evaluated using Arrhenius equation.

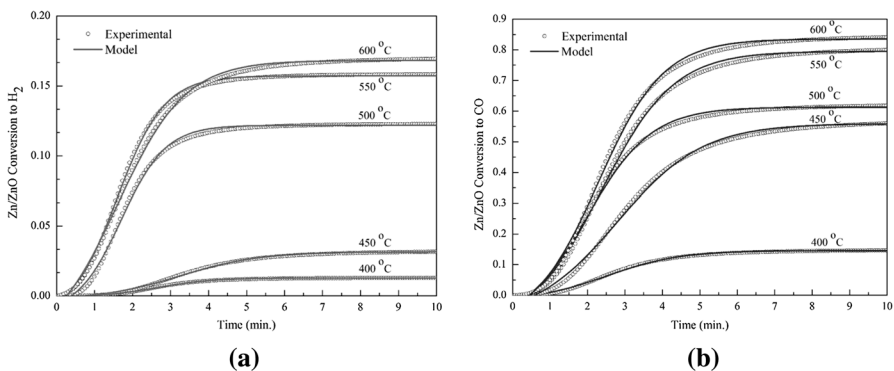


Fig. 5 Comparison of experimental and modelled solid conversions of Zn to ZnO for H_2 and CO at various temperatures

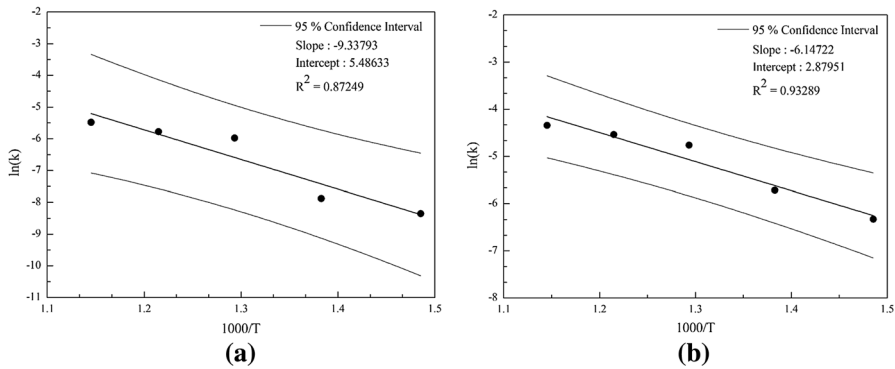


Fig. 6 Comparison of solid conversion to H₂/CO between the experimental and mathematical model for H₂O/CO₂-splitting at temperatures varied from 400, 450, 500, 550, and 600 °C

$$\frac{dX}{dt} = k(T) \cdot f(X), \quad k(T) = k_0 \cdot e^{-\frac{E_a}{RT}} \quad (25)$$

where X stands for solid conversion, t is the reaction time (s), f(X) is a function of reaction rate of the conversion. The logarithm plot of the Arrhenius equation ($\ln k(T) = \ln k_0 - E_a/RT$) are shown in Fig. 6, where slope of $\ln k(T)$ vs. $1/T$ was the apparent activation energy (E_a) and y-intercept was the pre-exponential factor (k_0). E_a of H₂O and CO₂ splitting was 77.63 and 51.11 kJ/mol, respectively, while k_0 was 4.02 and 0.30 s⁻¹.

Conclusion

The conversions of Zn to ZnO increased with increasing temperature. The H₂O and CO₂ co-splitting was occurred in 2 different mechanistic zones at below 550 (called surface reaction) and above 550 °C (called core-cracking/shrinking). CO₂ competed H₂O in adsorption/dissociation, agreeing with the kinetics data. The mathematical model using Boltzmann equation was found to correspondingly support the experimental-based solid conversion. The apparent activation energy for H₂O/CO₂ splitting on Zn/ZnO was estimated at 77.63 and 51.11 kJ/mol, respectively. Pre-exponential factor for H₂O and CO₂ splitting was 4.02 and 0.30 s⁻¹.

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