Exploiting kinetics to unravel the role of a ZnO diluent in the production of CO via oxidizing Zn particles with CO_2

David Weibel, Zoran R. Jovanovic *, Aldo Steinfeld

ETH Zurich, Department of Mechanical and Process Engineering, Sonneggstrasse 3, 8092 Zurich, Switzerland

HIGHLIGHTS

- Thermogravimetric study of the reaction of Zn and CO_2 in the presence of ZnO.
- Modelling kinetics of gas-solid reactions.
- Direct oxidation of pure Zn particles is inhibited by impervious ZnO product scale.
- Heterogeneous reaction of $Zn_{(g)}$ and CO_2 on ZnO surface promotes Zn sublimation.
- Higher Zn sublimation rates render ZnO product scale more permeable.

GRAPHICAL ABSTRACT
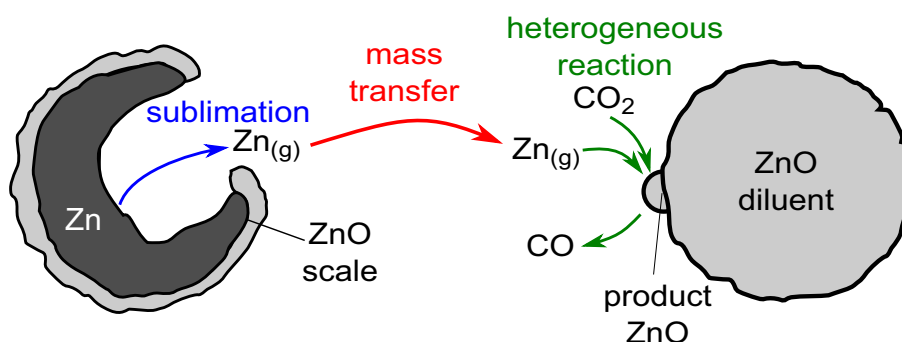
ABSTRACT

Direct oxidation of pure Zn particles with CO_2 is inhibited by an impervious ZnO scale. The presence of a ZnO diluent surface provides a site for an additional heterogeneous reaction of sublimated Zn that allows for a fast and high conversion of Zn. This is relevant to the efficient production of CO by the oxidation of Zn particles produced by the solar thermal dissociation of ZnO that are generally contaminated by the recombined ZnO. The overall reaction mechanism thus involves the sublimation of $Zn_{(g)}$ from the Zn surface, its transport to the ZnO diluent surface, and its subsequent heterogeneous reaction with CO_2 on this surface. To elucidate the most relevant of those elementary steps different kinetic models were tested against a broad set of isothermal thermogravimetric data acquired at different temperatures, CO_2-concentrations, and initial ZnO contents. The overall rate was found to be controlled by the transport of $Zn_{(g)}$ to the ZnO diluent surface and the reaction of the chemisorbed CO_2 either with $Zn_{(g)}$ or with Zn incorporated from gas phase into the ZnO lattice surface sites. Increasing the initial content of ZnO diluent increases the effectiveness of the heterogeneous reaction at the ZnO diluent surface which facilitates the sublimation of Zn and appears to render the ZnO product scale surrounding unreacted Zn more permeable.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Because of its high O_2 looping capacity per unit mass the Zn/ZnO thermochemical redox has been considered an attractive

path to producing renewable fuels from H_2O and CO_2 (Loutzenhiser et al., 2010; Steinfeld, 2002). This cycle is initiated by the highly endothermic thermal dissociation of ZnO at temperatures in the vicinity of 1800 °C that are achieved using concentrated solar radiation as the source of heat (Schunk et al., 2008; Villasmil et al., 2013). The dissociation yields a gaseous mixture of Zn and O_2 (Eq. (1)) that is rapidly quenched to suppress product
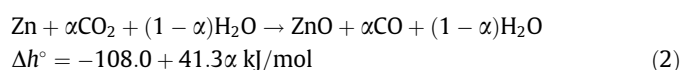
---

* Corresponding author.
E-mail address: zjovanovic@ethz.ch (Z.R. Jovanovic).

Nomenclature

a_i	specific BET surface area of species i [m²/kg]
c_i	molar concentration of gaseous species i [mol/m³]
$\bar{c}_i$	molar concentration of gaseous species i at the ZnO surface [mol/m³]
c_{Zn}^*	equilibrium concentration of $Zn_{(g)}$ [mol/m³]
d	volume-based mean particle diameter [m]
$\Delta h°$	standard molar enthalpy of reaction [J/mol]
k	apparent reaction rate constant [–]
k_{mt}	apparent mass transfer coefficient [m/s]
k_i^a	rate constant for adsorption of species i on the ZnO surface [m³/s]
k_i^d	rate constant for desorption of species i from the ZnO surface [mol/s]
k_i^{ox}	rate constant for oxidation step according to mechanism m [m³/s or m²/mol]
k^{ox}	apparent rate constant of the heterogeneous reaction of $Zn_{(g)}$ and CO_2 on the ZnO surface defined by Eq. (39) [m/s]
K_i^a	equilibrium adsorption constant for species i [m³/mol]
m	temporal sample mass [kg]
m_0	initial sample mass [kg]
m_f	sample mass after complete oxidation [kg]
M_i	molar mass of species i [kg/mol]
n	temporal molar amount of Zn [mol]
n_0	initial molar amount of Zn [mol]
$\dot{n}_{sub}$	molar rate of sublimation of Zn [mol/s]
$\dot{n}_{mt}$	molar rate of $Zn_{(g)}$ transport from the Zn surface to the ZnO surface [mol/s]
$\dot{n}_{rxn}$	molar rate of the heterogeneous reaction of $Zn_{(g)}$ and CO_2 on the ZnO surface [mol/s]
N^*	total number of CO_2 and CO adsorption sites on the ZnO surface per unit surface area of ZnO [1/m²]
$N^\#$	total number of Zn adsorption sites on the ZnO surface per unit surface area of ZnO [1/m]
r_{rxn}	rate of the heterogeneous reaction of $Zn_{(g)}$ and CO_2 on the ZnO surface per unit ZnO surface area [mol/(m²·s)]
$r_{rxn,i}$	rate of the step i of the heterogeneous reaction of $Zn_{(g)}$ and CO_2 on the ZnO surface per unit ZnO surface area [mol/(m²·s)]

p_{Zn}^*	equilibrium partial pressure of Zn [Pa]
R	universal gas constant [J/(mol·K)]
s_{Zn}	temporal surface area of the Zn surface per initial number of moles of Zn [m²/mol]
S_i	surface area of solid i [m²]
t	time [min]
t_{preox}	duration of the Zn pre-oxidation procedure [min]
T	temperature [°C]
w_{ZnO}	initial mass fraction of ZnO in a blend [wt%]
W_{ZnO}	initial ZnO-to-Zn mass ratio in a blend [–]
x_i	mole fraction of gaseous species i [%]
X	conversion of Zn [–]
y	spatial coordinate [m]

Greek symbols

α	CO_2 molar fraction in the stoichiometric oxidation of Zn in CO_2 and H_2O [–]
η	lumped parameter defined by Eq. (39) [–]
θ_i^*	fraction of CO/CO_2 adsorption sites the diluent ZnO surface occupied by species i [–]
$\theta_{Zn}^\#$	fraction of occupied Zn adsorption sites on the diluent ZnO surface [–]
θ^*	fraction of free CO/CO_2 adsorption sites on the diluent ZnO surface [–]
$\theta^\#$	fraction of free Zn adsorption sites on the diluent ZnO surface [–]
κ	$Zn_{(g)}$ mass transfer coefficient defined by Eq. (9) [m³/(mol s)]
λ	lumped conversion rate parameter as defined in Eq. (42) [m³/(mol s)]
ξ	fraction of the ZnO diluent surface participating in the heterogeneous reaction [–]
φ	effectiveness factor for the heterogeneous reaction (a measure of how much the reaction rate is lowered by the pore diffusion) [–]

recombination and maximize the yield of solid Zn (Villasmil et al., 2013). However, as achieving the required rapid quench rates is both technically challenging and costly, the solid product known as "solar Zn" generally contains a substantial amount of ZnO (Abanades, 2012; Gstoehl et al., 2008; Schunk et al., 2008). In the final step summarized by Eq. (2), the solar Zn is exposed to CO_2 and/or H_2O, when it reacts exothermically to produce fuel (CO and/or H_2) and ZnO. The ZnO is then returned to the reduction step to continue the cycle.

$$ZnO \rightarrow Zn + 0.5\,O_2$$
$$\Delta h° = 350.5 \text{ kJ/mol} \tag{1}$$

$$Zn + \alpha CO_2 + (1-\alpha)H_2O \rightarrow ZnO + \alpha CO + (1-\alpha)H_2O$$
$$\Delta h° = -108.0 + 41.3\alpha \text{ kJ/mol} \tag{2}$$

Previous studies of the oxidation of pure Zn particles (Eq. (2)) revealed that an impervious ZnO layer developing over the Zn surface eventually ceases further oxidation at impractically low conversions (Loutzenhiser et al., 2009; Nakamura et al., 2007). This observation has led some researchers to suggest oxidizing Zn either in the liquid phase (Berman and Epstein, 2000) or as aerosol nano-particles precipitated from the vapor (Ernst et al., 2006;

Melchior et al., 2009; Venstrom and Davidson, 2013; Wegner et al., 2006). However, either of these alternative approaches requires additional energy to melt and/or vaporize Zn which decreases the work that can be extracted from the produced fuel per total energy input (Steinfeld, 2002). Additionally, handling Zn as either a liquid or vapor requires the use of unconventional reactor concepts that are hard to operate and/or scale-up (Berman and Epstein, 2000; Ernst et al., 2006; Melchior et al., 2009; Venstrom and Davidson, 2013; Wegner et al., 2006).

Curiously, the contamination of solar Zn with recombined ZnO was found to facilitate oxidation reactions at temperatures below the melting point of Zn (420 °C) and enable complete Zn conversion within a few minutes (Abanades, 2012; Stamatiou et al., 2013). This reaction time is still considerably longer than that required for oxidizing Zn vapor (1–2 s) (Venstrom and Davidson, 2013). However, the difference in reaction times is compensated for by the disparity in the feedstock densities, such that the size of a conventional gas-solid reactor required to completely convert the solid solar Zn is roughly the same as a reactor which utilizes Zn vapor as feedstock (Weibel et al., 2014).

The facilitating role of ZnO in Zn oxidation is attributed to a complex multi-step reaction mechanism first speculated by Stamatiou et al. (2013) and then refined by Weibel et al. (2014).