



ELSEVIER

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Mechanisms of hydrolysis in a transverse jet zinc aerosol reactor

Julia Haltiwanger Nicodemus^{a,*}, Jane H. Davidson^b^a Engineering Studies, Lafayette College, Easton, PA, United States^b Mechanical Engineering, University of Minnesota, Minneapolis, MN, United States

HIGHLIGHTS

- Hydrolysis of zinc particles in a transverse jet aerosol reactor is investigated.
- Particle deposition on the wall of the reactor is completely eliminated.
- Zinc particles grow by condensation to 300 nm to 1 μm.
- Overall conversions are dominated by the heterogeneous hydrolysis of Zn vapor.
- The work brings to light the role of Zn vapor in hydrolysis in aerosol reactors.

ARTICLE INFO

Article history:

Received 23 June 2014

Received in revised form

1 October 2014

Accepted 6 October 2014

Available online 16 October 2014

Keywords:

Solar energy

Fuel

Hydrolysis

Thermochemical cycle

Aerosol

Metal oxidation

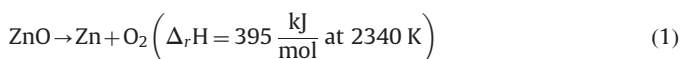
ABSTRACT

The mechanisms of hydrolysis of zinc particles formed and entrained in a reacting gas flow were explored. Experiments were carried out in a transverse jet reactor designed for nucleation of Zn nanoparticles via a rapid quench followed by reaction at temperatures from 418 to 713 K. The aerosol particles were collected on a filter and characterized via X-ray diffraction and scanning electron microscopy. Even for quench rates as high as 10^4 K/s, nucleation of Zn vapor was incomplete. With a quench of Ar at temperatures less than the saturation temperature of Zn, 1 to 3 μm hour-glass shaped hexagonal Zn particles were formed, consistent with formation via 2-D layer by layer by condensation and subsequent evaporation. Above the saturation temperature, Zn nanowires were formed from the vapor phase on the filter surface. With a steam quench, particles remained hexagonal but were generally smaller, from 300 nm to 1 μm across the hexagonal face. Above 573 K, a shell of ZnO impeded evaporation of particles. Overall conversion of Zn to ZnO was dominated by the heterogeneous hydrolysis of Zn vapor, not hydrolysis of Zn particles. These results shed light on the mechanisms of particle growth and hydrolysis in Zn aerosol reactors. In particular, the finding that hydrolysis is dominated by a heterogeneous reaction between Zn(*v*) and steam is of critical importance to developing better approaches to react the Zn with steam, supporting prior work that shows that the heterogeneous vapor phase reaction is kinetically favored over the diffusion limited conversion of solid or liquid Zn particles.

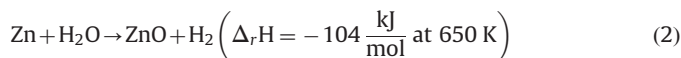
© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The two step zinc (Zn)/zinc oxide (ZnO) solar thermochemical hydrogen production cycle consists of the thermal dissociation of ZnO:



and the exothermic hydrolysis of Zn with steam (H_2O) to produce ZnO and hydrogen (H_2):



Ideally, ZnO is dissociated in the solar-driven reaction (1) and ZnO produced in the non-solar reaction (2) is cycled back to the first step, so that the net effect is the splitting of water. In this paper, we focus on the challenges of reaction (2). Prior work has shown that kinetics are slow for hydrolysis of solid or liquid Zn particles due to the formation of a ZnO layer on the surface through which the reactants must diffuse (Delalu et al., 2000; Alimenti et al., 2004; Bazan et al., 1999; Berman and Epstein, 2000; Weidenkaff et al.,

* Corresponding author. Tel.: +1 610 330 5228.

E-mail address: nicodemj@lafayette.edu (J.H. Nicodemus).

2000). Much attention has been given to reacting aerosols of Zn nanoparticles as a solution to this challenge (Weiss et al., 2005; Wegner et al., 2006; Ernst et al., 2006; Melchior et al., 2009; Abu Hamed et al., 2007, 2009; Funke et al., 2008; Ernst et al., 2009; Vishnevsky and Epstein, 2007; Park et al., 2005; Rai et al., 2006). The high specific surface area was expected to favor high rates of mass transfer and favorable hydrolysis kinetics. The concept is to rapidly quench Zn vapor in order to nucleate high concentrations of nano-scale particles, hydrolyze them, and recover the ZnO particles from the gas stream in a continuous process (for example via filtration). To date, conversion of Zn aerosol particles to ZnO has not shown great promise. Kinetics have not been fast enough for significant conversion, and particle deposition on the heated walls of aerosol reactors has precluded continuous recovery of the ZnO for cycling back to reaction (1) (Weiss et al., 2005; Wegner et al., 2006; Ernst et al., 2006; Melchior et al., 2009; Abu Hamed et al., 2007; Funke et al., 2008; Abu Hamed et al., 2009). Moreover, particle deposition on reactor walls has, to some extent, obscured the mechanisms of particle growth and hydrolysis. In addition, nucleation requires significant quenching gas flow rates. Consideration of the energy requirements to produce and heat the quench gas required for Zn aerosol nucleation has not been considered in prior work but may be mitigated through recuperating the sensible heat in the effluent to preheat the quench gas.

In the evaporation/condensation process the metal precursor material, evaporated and carried through a reactor by an inert gas, undergoes rapid controlled quenching. In the quenching process, evaporated metal atoms lose kinetic energy through collisions with inert-gas atoms, leading to a high degree of supersaturation. Supersaturation is defined by the saturation ratio, S' , the ratio of monomer concentration to the monomer concentration at saturation. The critical cluster size, d^* , is the size at which the evaporation rate and the condensation rate are balanced. Monomer clusters with diameter equal to or greater than the critical diameter form stable particles. Because d^* is inversely proportional to $\ln S'$, when the metal vapor suddenly reaches high degrees of supersaturation, the corresponding critical diameter becomes very small. A nearly instantaneous “nucleation event” occurs as a result (Girshick and Chiu, 1989).

Because the degree of supersaturation achieved determines the primary particle size, process parameters that result in higher saturation ratios lead to smaller primary particles. Fast quench rates are generally expected to result in higher saturation ratio peak values and thus the formation of high concentrations of small particles (Girshick and Chiu, 1989; Granqvist and Buhrman, 1976; Panda and Pratsinis, 1995; Pratsinis, 1988; Pratsinis and Vemury, 1996; Joshi et al., 1990; Suryanarayana and Prabhu, 2007; Mahoney and Andres, 1995; Backman et al., 2002). However, local temperatures and vapor concentrations are also important factors in particle formation (Liu and Garrick, 2012). In classical nucleation theory, the surface tension is an important parameter affecting the nucleation rate and critical cluster size. Recent work incorporates a size-dependent surface tension model to predict nucleation rates for Zn entrained in a jet issuing into a parallel flow. The model data implies that at the temperatures and concentrations predicted by models of our reactor (Nicodemus and Davidson, 2012), we can expect peak nucleation rates on the order of $10^{16}/\text{cm}^3 \text{ s}$ at the edge of the jet and $10^{14}/\text{cm}^3 \text{ s}$ at the center of the jet (Liu and Garrick, 2012). Their work also suggests that Zn may have a maximum nucleation rate, and that increasing quench rates beyond that threshold can actually decrease Zn particle nucleation (Liu and Garrick, 2012).

There are two primary paths for nanoparticle nucleation and growth. The first path occurs if a significant majority of the Zn vapor nucleates into particles during the quenching process. In this case, high concentrations of nano-sized particles are produced. These

particles grow by coagulation, and if the resulting agglomerates do not coalesce, high specific surface area is maintained for hydrolysis. It is expected that coalescence is inhibited if the particles are encased in a shell of ZnO, due to the significantly higher melting temperature of ZnO. The second path occurs if a significant fraction of the Zn mass remains in the vapor phase after particle nucleation. In this case, particles grow by condensation as the Zn vapor condenses in layers on the nucleated particles. Growth by condensation results in larger particles at lower concentration than via the first path.

There are three potential mechanisms for H_2 production in the aerosol reactor. At temperatures below 423 K and for 70 nm particles, Zn has been observed to react with two steam molecules to form $\text{Zn}(\text{OH})_2$ and H_2 (Ma and Zachariah, 2009). Although ZnO is not produced in this reaction, a second reaction is initiated when the $\text{Zn}(\text{OH})_2$ is exposed to slightly elevated temperatures (above 423–438 K), resulting in decomposition of the $\text{Zn}(\text{OH})_2$ into ZnO and H_2O . The ZnO produced in the second reaction can be used in the solar step, closing the cycle. At temperatures above 573 K, Zn particles can react directly with steam in either a fast, surface reaction, or a much slower, diffusion limited reaction (Ernst et al., 2009). If Zn(g) remains in the aerosol reactor because particle growth is dominated by condensation, the remaining Zn (ν) could react with steam on available surfaces via heterogeneous Zn vapor hydrolysis, including the surface of aerosol particles (Clarke and Fray, 1979).

Prior work has demonstrated the kinetics of heterogeneous hydrolysis is orders of magnitude faster than diffusion limited hydrolysis (Venstrom and Davidson, 2013; Clarke and Fray, 1979, 1975). A thermodynamic analysis of the full cycle found that achieving complete conversion of Zn to ZnO via the heterogeneous hydrolysis reaction raised practical efficiencies from 6% (due to low conversions in the aerosol process) to 27% without heat recuperation, despite the elevated temperatures needed for the hydrolysis reaction. With heat recuperation, the theoretical maximum efficiency increases to 38% (Venstrom and Davidson, 2011).

In the present study, we explore the pathways for particle formation, growth, and hydrolysis in a transverse jet reactor, designed to reduce particle deposition on the heated walls while maintaining a quench rate of $2 \times 10^4 \text{ K/s}$, on the high end of past reactors that were reported to generate and react Zn particles (Nicodemus and Davidson, 2012). The transverse jet reactor is the only reactor to eliminate particle deposition in the reaction zone and that allows particle nucleation and growth to proceed at $\sim 450 \text{ K}$ for an average residence time of $\sim 3 \text{ s}$ before temperatures are elevated to levels favorable for hydrolysis of Zn particles. Particle residence times at temperatures favorable for Zn hydrolysis are $\sim 5 \text{ s}$. Because of these favorable attributes of the reactor, we are able to distinguish heterogeneous hydrolysis of Zn from the diffusion limited reactions assumed in prior work. The finding that hydrolysis is dominated by a heterogeneous reaction between Zn(ν) and steam is critically important in developing better approaches to react the Zn with steam. We present a series of experiments conducted over a range of temperatures and partial pressures of Zn and H_2O to gain a more complete understanding of the mechanisms of conversion of Zn to ZnO in the aerosol.

2. Experimental method

2.1. Reactor

The transverse jet reactor and instrumentation are depicted in Fig. 1. The reactor design, control, and monitoring are described in greater detail in prior work (Nicodemus and Davidson, 2012). The reactor consists of five sections: the pre-heat zone, the evaporation

Download English Version:

<https://daneshyari.com/en/article/6590791>

Download Persian Version:

<https://daneshyari.com/article/6590791>

[Daneshyari.com](https://daneshyari.com)