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Oxidation of copper at high temperature as an example for gas-solid reactions in a downer reactor – experiments and model-based analysis

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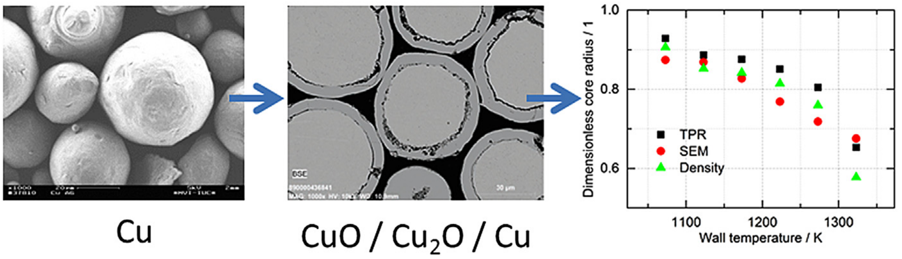
HIGHLIGHTS

- Oxidation of copper particles was studied in a downer reactor at 1073 – 1323 K.
- Product layers were distinguished and analysed by XRD, EDX, SEM, TPR and density.
- Validity of the approach was assured by independent oxygen analysis.
- A 2-phase 1D-model for the downer reactor at high temperatures was developed.
- Solid state diffusion data was obtained and compared to the literature.

GRAPHICAL ABSTRACT



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ABSTRACT

The kinetics of a gas-solid reaction at high temperatures were studied in a downer reactor of 2.8 m length. As an example, the oxidation of copper particles was carried out at different wall temperatures (1073 K–1323 K), oxygen concentrations (14 Vol.-%–67 Vol.-%), and particle diameters (51 µm–156 µm). Although the residence time of the particles was of the order of 1–4 s only, considerable copper conversions could be achieved. XRD, EDX and SEM analysis of the formed products revealed that single layer formation of cuprous oxide prevails up to oxygen concentrations of about 25 Vol.-%. At higher oxygen concentrations, double layer oxidation occurs with a second cupric oxide layer forming on top of cuprous oxide. The remaining core radius of unreacted copper was determined through a combination of density measurements, analysis of TPR spectra, and direct SEM observation. Although significant scattering of the individual measurements was observed, it could be shown by independent elemental analysis of the products that the average values from all measurements are reliable. For quantitative evaluation of the measurements we developed a one-dimensional downer reactor model which allowed to calculate the residence time and particle temperature as a function of reactor length. Using this information we derived solid state diffusion coefficients, the activation energies of which agreed well with literature data. Overall it could be shown that the progress of a gas-solid reaction in a downer reactor can be successfully described with a combination of experimental methods and subsequent model-based data analysis.

1. Introduction

During the 1970s the so-called fluidized bed downer was developed as a new reactor concept by the oil and gas industry (Zhu et al., 1995; Cheng et al., 2008). In this reactor both solid and gas

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Nomenclature

a_{gp}	specific surface area between gas and particles, $(1-\varepsilon_g)\cdot 6/d_p$, m^2/m^3
a_{gw}	specific surface area between gas and wall, $4/d_R$, m^2/m^3
a_{pw}	specific surface area between particles and wall, $4/d_R(1-\varepsilon_g)$, m^2/m^3
c	oxygen concentration in the gas phase, mol/m^3
c_p	specific heat capacity, J/(kg K)
C_w	drag coefficient, 1
$D(\mathrm{v},50)$	mean particle diameter of the particle size distribution Q_3, μm
D_{eff}	effective diffusion coefficient, m^2/s
d_p	particle diameter, m
d_R	reactor diameter, m
F	term of the momentum balance, kg/(m s^2)
F_{ij}	factor in Wilke's mixing rule, 1
$F_{i\text{-}j}$	solid flux, kg/(m^2 s)
g	gravitational constant, m^2/s
G_s	solid flux, kg/(m^2 s)
h	convective heat transfer coefficient, W/(m^2 K)
$\Delta_{rct}H$	reaction enthalpy of copper oxidation to Cu_2O, J/mol
L_R	length of the reactor, m
M	molar mass, g/mol
m_i	mass of the species i (Cu, Cu_2O, CuO), kg
$m_{O,sample}$	mass of oxygen in the sample, kg
$\dot{n}$	molar flow rate, mol/s
N_p	number of particles in a given sample mass
Nu	Nusselt number, 1
p	pressure, Pa
p_{O2}	partial pressure of oxygen in the reacting atmosphere, Pa
Pr	Prandtl number, 1
r	particle volume related reaction rate, $\left(-\frac{\nu_1}{\nu_2}\right)\tilde{\rho}_p u_p \cdot \frac{6}{d_p}\frac{dr_c}{dz}$, mol/(m^3 s)
R_0	initial particle radius, m
r_c	core radius, m
r_{ol}	radius at the boundary between the two oxide layers, m
Re	Reynolds number: $d_R \cdot u_{g,sup} \cdot \rho_g/\eta_g$
Re_p	particle Reynolds number: $d_p \cdot \vert u_{g,real} - u_p \vert \cdot \rho_g/\eta_g$
t	time, s
T	temperature, K
u	velocity, m/s
$\dot{V}$	volume flow rate, m^3/s
V_i	volume of species i (Cu, Cu_2O, CuO), m^3
y_{O2}	molar fraction of oxygen in the reacting atmosphere
z	axial distribution variable, m
Z	dimensionless radius, 1

Greek letters

ε	hold-up
ϵ	emissivity
η	dynamic viscosity, Pa s
λ	thermal conductivity, W/(m K)
ν	stoichiometric coefficient
π	3.1415
ρ	density, kg/m^3
$\tilde{\rho}$	molar density, ρ/M, mol/m^3
σ	Stephan-Boltzmann constant, W/(m^2 K^4)
τ	time for complete conversion of the solid, s
ϕ	copper content in cuprous oxide, g/g
χ	copper content in cupric oxide, g/g

Subscripts

0	initial state
aux	auxiliary volume stream
c	core
conv	convective heat transfer
D	drag
Diff	limitation due to diffusion
F	friction
g	gas phase
mix	gas mixture
O_2	oxygen
ol	oxide layer
p	particle
P→E	particle to reactor entrance / exit
P→W	particle to wall
ph	preheated volume stream
r	radiation
R	resitance
real	real (gas velocity)
s	solid
STP	standard temperature and pressure
sup	superficial (gas velocity)
w	wall

Abbreviations

EDX	energy dispersive X-ray spectroscopy
HT	heat transfer
IGFID	inert gas fusion infrared detection
PSD	particle size distribution
STP	standard temperature and pressure (101325 Pa, 273.15 K)
SEM	scanning electron microscopy
ODE	ordinary differential equations
TCD	thermal conductivity detector
TPR	temperature programmed reduction
XRD	x-ray diffraction

phase are flowing co-currently in the direction of the gravity force. This results in several advantages compared to the standard circulating fluidized bed riser reactor such as avoidance of back-mixing phenomena, creation of a narrow residence time distribution (RTD) and enabling of short contact times between the phases (Wei et al., 1995; Zhang et al., 2001).

Several studies have been devoted to the application of downer reactors in fluid catalytic cracking processes (Zhu et al., 1995; Cheng et al., 2008). Here, the short contact times permit the direct choice of the product chain length. Other applications are related to the thermal treatment of coal such as partial oxidation (Kim et al., 2001) and pyrolysis (Wang et al., 2005; Dong et al., 2012; Zhang et al., 2013). Further extensive studies cover hydrodynamics, especially the mixing behaviour (Wei et al., 1994; Bang et al., 1999), radial profiles of the solid holdup (Bai et al., 1991; Lehner and Wirth, 1999; Zhang et al., 2003; Qi et al., 2008), the solids circulation rate (Ball and Zhu, 2001; Chen and Li, 2004) and the RTD behaviour of the downer reactor (Brust and Wirth, 2004).