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Simulation of the catalyzed isotopic exchange between hydrogen and water in a trickle bed reactor

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HIGHLIGHTS

- Limiting step of overall isotopic exchange alters near bottom of the reactor.
- Molar flow rate ratio in feed and dilution ratio in catalyst bed are optimized.
- Hydrogen humidifying affects deuterium removal in hydrogen.

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ABSTRACT

The catalytic exchange column of countercurrent trickle bed for deuterium removal from hydrogen is simulated based on experimental results along with established reaction and mass transfer models, accounting for the humidification of hydrogen in a catalyst bed filled with platinum/styrene-divinylbenzene copolymer pellets and Dixon rings. Relative deviations of less than 30% are achieved between the experimental and the simulated HD molar fractions at the column outlet. Simulation results indicate that hydrogen humidification exerts a noticeable influence on gas and liquid phase flow rates, leading to an overestimated removal percentage of deuterium when such flow rate variances are neglected. Rate limiting step for the overall gas-liquid isotopic exchange is discussed. Finally, the operation conditions are optimized using the developed model.

1. Introduction

Catalyzed isotopic exchange between hydrogen and water is an effective method for separating hydrogen isotopes during waste water treatment of future fusion reactors and heavy water upgrading of fission reactors (Alekseev et al., 2002; Ionita et al., 2015; Vasyanina et al., 2008). Some matured methods such as liquid phase catalytic exchange (LPCE) and combined electrolysis and catalytic exchange (CECE) have been recognized as prospective tritiated water treatment techniques for the International Thermonuclear Experimental Reactor (ITER) (Ana et al., 2009; Ionita et al., 2015). Alekseev et al. (2011) produced highly purified heavy water and deuterium gas in a pilot CECE plant for heavy water upgrading and detritiation.

The overall process of catalyzed isotopic exchange between deuterated hydrogen and water (Eq. (1)) can be divided into two steps: catalytic exchange in gas phase (Eq. (2)) and gas-liquid mass transfer of HDO (Eq. (3)) (Ovcharov et al., 2009).

$$HD_{(g)} + H_2O_{(l)} \rightleftharpoons H_{2(g)} + HDO_{(l)} \quad (1)$$

$$HD_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + HDO_{(g)} \quad (2)$$

$$HDO_{(g)} + H_2O_{(l)} \rightleftharpoons H_2O_{(g)} + HDO_{(l)} \quad (3)$$

Noble metals presented high catalytic activities for the isotopic exchanges merely in gas phase, which therefore made the process for gas-liquid isotopic exchange complicated (Kumar et al., 2013; Ye et al., 2013). Stevens (1972) designed the first hydrophobic catalyst for combining gas-liquid mass transfer and catalytic exchange in a catalytic exchange column of a countercurrent flow trickle bed (Kumar et al., 2013). Gas-liquid mass transfer in catalyst bed was enhanced by mixing hydrophilic packing with hydrophobic catalyst (Ye et al., 2014).

Simulation of the catalytic exchange column, which is the main facility of LPCE and CECE, is important for the design and optimiza-

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Nomenclature

a	interfacial area (m^{-1})
A	cross sectional area of column (m^2)
C	molar concentration ($mol \cdot m^{-3}$)
Cp	heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$)
D	diffusivity ($m^2 \cdot s^{-1}$)
d	nominal diameter (m)
d_i	inner diameter of reactor (m)
D_a	axial dispersion coefficient ($m^2 \cdot s^{-1}$)
e	ratio of gas and liquid molar flow rates (dimensionless)
F	molar flow rate ($mol \cdot s^{-1}$)
g	acceleration of gravity ($m \cdot s^{-2}$)
$Ga = \frac{d^3 g \rho_L^2}{\mu_L^2}$	Galileo number (dimensionless)
h	heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
H	humidity (dimensionless)
ΔI_V	vaporization heat of liquid water ($J \cdot kg^{-1}$)
I	enthalpy ($J \cdot kg^{-1}$)
K_i	adsorption equilibrium constant for species i (Pa^{-1})
K_r	equilibrium constant for catalytic exchange (dimensionless)
k	rate constant for catalytic exchange in gas phase ($mol \cdot m^{-3} \cdot s^{-1}$)
k_{ps}	pseudo-first-order rate constant for catalytic exchange in gas phase (s^{-1})
k_m	molar mass transfer coefficient ($mol \cdot m^{-2} \cdot s^{-1}$)
k_H	weight mass transfer coefficient for humidification ($kg \cdot m^{-2} \cdot s^{-1}$)
L	liquid mass flow rate ($kg \cdot s^{-1}$)
m	gas-liquid equilibrium constant for HDO (dimensionless)
M	molar mass ($kg \cdot mol^{-1}$)
N_{HDO}	gas-liquid mass transfer rate of HDO ($mol \cdot m^{-3} \cdot s^{-1}$)
P	pressure (Pa)
$Pr = \frac{Cp\mu}{\lambda}$	Prandtl number (dimensionless)
Q	hydrogen volume flow rate ($Nm^{-3} \cdot s^{-1}$)
q	heat transfer rate (W)
r_{HD}	apparent catalytic exchange rate in gas phase for a unit volume of catalyst pellets ($mol \cdot m^{-3} \cdot s^{-1}$)
$r_{HD,b}$	apparent catalytic exchange rate in gas phase for a unit packed bed volume ($mol \cdot m^{-3} \cdot s^{-1}$)
$r_{HD,s}$	intrinsic catalytic exchange rate for a unit volume of catalyst pellets ($mol \cdot m^{-3} \cdot s^{-1}$)
R	universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)
$Re = \frac{du\rho}{\mu}$	Reynolds number based on superficial velocity (dimensionless)
$Re' = \frac{du'\rho}{\mu}$	Reynolds number based on relative velocity between gas and liquid phases (dimensionless)
$Sc = \frac{\mu}{D\rho}$	Schmidt number (dimensionless)
T	temperature (K)
u	superficial velocity ($m \cdot s^{-1}$)
$u' = \frac{u_L}{\beta_L} + \frac{u_G}{\beta_G}$	relative velocity between gas and liquid phases ($m \cdot s^{-1}$)
V	hydrogen mass flow rate ($kg \cdot s^{-1}$)
X_c	volume fraction of catalyst in the bed (dimensionless)
x	liquid phase molar fraction (dimensionless)
Y	molar fraction in purified hydrogen (dimensionless)
y	gas phase molar fraction (dimensionless)
Z_b	total height of packed bed (m)
z	axial coordinate (m)

Greek letters

α	relative volatility (dimensionless)
β	holdup (dimensionless)
δ	fitting parameter for liquid phase mass transfer coefficient (dimensionless)
ϕ	Thiele modulus (dimensionless)
ε	bed voidage (dimensionless)
η_i	catalytic effectiveness factor for internal diffusion (dimensionless)
η_t	overall catalytic effectiveness factor (dimensionless)
λ	thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
μ	viscosity (Pa·s)
θ_c	porosity of catalyst (dimensionless)
ρ	density ($kg \cdot m^{-3}$)
$\rho_{b,c}$	bed density of catalyst ($kg \cdot m^{-3}$)
χ	modifying factor for gas phase mass transfer coefficient (dimensionless)

Subscripts and superscripts

b	packed bed
c	catalyst
ca	calculated
e	effective
ex	experimental
G	gas phase
gs	gas-solid
gl	gas-liquid
H_2	hydrogen
H_2O	water
HD	deuterated hydrogen
HDO	deuterated water
k	fitting parameter number for liquid phase mass transfer coefficient (= 1, 2, 3, 4)
K	Knudsen
L	liquid phase
max	maximum
p	hydrophilic packing
po	pore
S	solid
t	total
V	vapor
w	wall
y	overall coefficient based on gas phase molar fraction
θ	standard state
$\rightarrow$	forward
$\leftarrow$	backward
$*$	equilibrium condition
0	feeding condition
1	outlet condition

tion of these processes. Previous simulations were based on conventional absorption column and trickle bed reactor models, e.g., Busigin (2015) used a mass transfer model in his LPCE column simulation with a large variance of deuterium atom fraction in feeding hydrogen. Sugiyama et al. (2011) utilized a channeling stage model to simulate LPCE column in the CECE process. However, the conventional gas-liquid mass transfer model cannot efficiently describe the overall isotopic exchange process described by Eq. (1) (Sugiyama et al., 2011), since the use of hydrophobic catalysts makes the wettability, reaction and mass transfer different from those of a conventional trickle bed filled with hydrophilic catalysts. Additionally, process complexity is also increased by coupling between the catalytic exchange in gas phase and the mass transfer accompanying phase change (Kumar et al., 2013). Gas humidification is a typical phase change in the industrial isotopic exchange process, but it is hardly accounted for in previous models.