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Modeling photocatalytic conversion of carbon dioxide in bubbling twin reactor

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ABSTRACT

The production of valued added fuels and chemicals via photocatalytic carbon dioxide reduction has attracted increasing attentions in recent years. Based on the traditional twin reactor configuration, a novel bubbling twin reactor is proposed to improve the conversion of carbon dioxide to methanol in this work. The multiphysical model for the bubbling twin reactor is developed and numerically simulated. The variations of the methanol production with the gas inlet flow velocity and gas inlet number are obtained. The results show that the bubbling twin reactor has a higher carbon dioxide conversion efficiency than the traditional one. Moreover, the methanol production subsequently increases as the gas inlet velocity increases. With the constant inlet gas volumetric flow rate, the production of methanol can be improved by increasing the gas inlet number.

1. Introduction

Global energy shortage and climate change have aroused wide public concerns, which motivate the researchers exploring the conversion of CO_2 to value-added chemicals and renewable fuels. In the past decades, various technologies of CO_2 reduction into hydrocarbon fuels have been deeply studied. As an eco-friendly way for CO_2 reduction and conversion, the photocatalytic method has received growing attentions since discovered for the first time in 1979 [1]. Baran et al. [2] pointed out that the conversion of CO_2 by solar energy is a realizable opportunity for the future. Moreover, Huang et al. [3] reported that the photocatalytic conversion of CO_2 into hydrocarbon fuels is a promising technology to resolve the energy shortage. Ola and Maroto-Valer [4] also concluded that the photocatalytic method is a realizable way to turn CO_2 into hydrocarbon fuel. Thampi et al. [5] found that the gas mixture of H_2 and CO_2 can react and form CH_4 by the catalytic of TiO_2. Kohno et al. [6] reported that the CO_2 can be reduced to CO by hydrogen on the photocatalyst of ZrO_2. Sato and White [7] declared that the water vapor can produce hydrogen by a catalytic reaction at room temperature. Shinichi and Ryota [8] investigated the photocatalytic reduction of carbon dioxide and hydrogen formation from water by experiments.

CO_2 can be reduced to hydrocarbons such as methanol (CH_3OH) by water after activating the photocatalyst of titanium dioxide (TiO_2) with light, which has been widely confirmed to be an alternative. However, the reduction efficiency is the main barrier for the application due to the poor reducibility of H_2O, leading to the low yield of hydrocarbons in the traditional photocatalytic reactor unexpectedly. Numerous researchers focused upon the efficiency improvement of this system by various approaches. Wang et al. [9] investigated the influence of the optical fiber installation on the system efficiency, finding that the methanol production efficiency decreases with increasing the optical fiber deviation from the monolith axis. Yuan et al. [10] studied the photocatalytic CO_2 reduction in the optical fiber monolith reactor with multiple inverse lights by the numerical methods. Tahir et al. [11] found that the photoactivity of metal-doped TiO_2 is affected by the electron transfer and illuminated surface area. Yuan et al. [12] proposed two optimized structures of optical fiber monolith reactor by adding reaction surfaces. On the other hand, Nong et al. [13] reported that the photochemical water splitting can lead to an efficiency improvement, which is regarded as a new idea for the combination of water photolysis (hill reaction) and photocatalytic CO_2 reduction. Lee et al. [14] proposed a novel twin reactor system for CO_2 photoreduction with a higher efficiency than the single one. The twin reactor integrates the water photolysis with the CO_2 photo-reduction, which can produce the higher methanol output rate due to the better reducibility of H_2

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Nomenclature

c	concentration, mol·m^{-3}
D	diffusion coefficient, m^2·s^{-1}
I	light intensity, W·m^{-2}
k	kinetic rate constant, m^4·s^{-1}·mol^{-2}
M	molecular weight, g·mol^{-1}
p	pressure, Pa
P	production, μmol
r	reaction rate, mol·m^{-3}·s^{-1}
R	perfect gas constant, 8.314 J·mol^{-1}·K^{-1}
t	time, s
T	temperature, K
V	molar volume, cm^3·mol^{-1}
N	mass transfer rate, mol·m^{-2}·s^{-1}
K	mass transfer coefficient, s·mol·kg^{-1}·m^{-1}
H	henry constant, Pa·m^3·mol^{-1}
ΔH	enthalpy change, kJ·mol^{-1}
ΔG	Gibbs free energy, kJ·mol^{-1}
E	ionic strength, mol·m^{-3}
z	ionic valence
h	solubility coefficient
e	energy coefficient
m	mass transfer, kg·m^{-2}·s^{-1}
S	area, m^2
$\vec{v}$	velocity, m·s^{-1}
$\vec{F}$	surface tension, Pa·m^{-1}
$\vec{a}$	surface normal
$\vec{g}$	acceleration of gravity, m·s^{-2}
Hr	local solar time
a	parameter of the fitting function
b	parameter of the fitting function
c	parameter of the fitting function
A	parameter of the fitting function
q	parameter of the fitting function
n	gas inlet number
d	diameter of the gas inlet, cm
R	radius of the cylindrical reactor, cm
L	height of the cylindrical reactor, cm
x	variable of the fitting function
y	variable of the fitting function

Greek letters

δ	film thickness, mm
ν	chemical calculated number
ρ	density, kg·m^{-3}
φ	correction coefficient of Henry constant
μ	volume-averaged viscosity, Pa·s
κ	curvature, m^{-1}
α	volume fraction
γ	surface tension coincident, Pa·m
θ	pitch, m
β	parameter of the fitting function

Subscript and superscript

L	liquid phase
G	gas phase
j	number of reaction or ion
i	number of reactant or ion
m	interface
q	number of phases

[15]. Cheng et al. [16] experimentally investigated the twin reactor, finding that too much CO as the co-feed can decrease the yield of CH_3OH adversely. Yu et al. [17] reported that the membrane resistance in the twin system cannot hinder photocatalytic water-splitting reaction. The processes of the CO_2 photoreduction are characterized by the feasible exothermic reactions, as shown in Table 1 [16]. Due to the ΔG^0 of reactions (a), (d) and (e) are less than 0, the reactions are spontaneous and thermodynamically favorable. Despite the reactions (b) and (c) are non-spontaneous, their positive ΔH^0 and ΔG^0 are still much lower than those of water photolysis reactions (ΔH^0 = 285.8 kJ/mol; ΔG^0 = 237.1 kJ/mol). Therefore, the photocatalysts photon energy can convert into chemical energy in the photoreaction system accompanied by the puny positive change in Gibbs free energy.

As is known, the traditional twin reactor consists of two reaction systems, between which an ion exchange membrane separates the photocatalytic water splitting and CO_2 reduction. The H^+ generated in the water photolysis reaction can be used by CO_2 photo-hydrogenation immediately with the light activation at the room temperature. Because of the better reducibility of H^+ than H_2O, the twin reactor has a higher CO_2 conversion efficiency. However, the poor mass transfer between the liquid and gas phases in the traditional twin reactor is a main barrier for the practical application. It is widely accepted that the interface area between the liquid and gas phases plays an important role in the mass transfer process [18]. Moreover, the bubble reactor is commonly adopted in chemical field, due to the high mass transfer rate [19] and low maintenance cost [20]. Therefore, a novel bubbling twin reactor is proposed in this study based on the traditional twin reactor, which can increase the interface area between the liquid and gas phases by producing bubbles. The hydrodynamics and mass transfer (CO_2 and CO) characteristics are gained by the CFD software FLUENT, and the photocatalytic water splitting and CO_2 reduction are numerically simulated by the multiphysics software COMSOL. Moreover, the effects of the gas inlet velocity and gas inlet number on the CH_3OH production are also discussed, which can contribute to the optimization of CO_2 photocatalytic reactor.

2. Computational models

The detailed hydrodynamics (continuity, momentum) and mass transfer (species transport) models in the bubbling twin reactor are developed by using the Representative Elementary Volume (REV) method, with the photocatalytic reactions introduced.

2.1. Physical model

The mass transfer and reaction processes in the bubbling twin reactor are schematically presented in Fig. 1, where A is the inlet gas (CO_2 & CO), B is the outlet gas (CO_2 & CO), C is the outlet gas (O_2), D is the valve, E is the nafion membrane, F is the H_2O splitting reactor, G is the CO_2 reduction reactor and H is the pressure gage. The bubbling twin

Table 1
Changes of enthalpy and Gibbs free energy in CO_2 photocatalytic reactions [16].

Reactions		ΔH^0 (kJ·mol^{-1})	ΔG^0 (kJ·mol^{-1})
(a)	$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l)$	−137.8	−10.7
(b)	$CO(g) + CH_3OH(l) \rightarrow HCOOCH_3(l)$	−25.6	6.6
(c)	$CO_2(g) + H_2(g) + CH_3OH(l) \rightarrow HCOOCH_3(l) + H_2O(l)$	−31.8	25.8
(d)	$HCOOCH_3(l) + 2H_2(g) \rightarrow 2CH_3OH(l)$	−99.7	−35.1
(e)	$HCOOCH_3(l) + CO(g) \rightarrow CH_3CHO(l) + CO_2(g)$	−96.5	−86.7