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Performance analysis of photocatalytic CO_2 reduction in optical fiber monolith reactor with multiple inverse lights

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ABSTRACT

Photocatalytic CO_2 reduction seems potential to mitigate greenhouse gas emissions and produce renewable energy. A new model of photocatalytic CO_2 reduction in optical fiber monolith reactor with multiple inverse lights was developed in this study to improve the conversion of CO_2 to CH_3OH. The new light distribution equation was derived, by which the light distribution was modeled and analyzed. The variations of CH_3OH concentration with the fiber location and operation parameters were obtained by means of numerical simulation. The results show that the outlet CH_3OH concentration is 31.1% higher than the previous model, which is attributed to the four fibers and inverse layout. With the increase of the distance between the fiber and the monolith center, the average CH_3OH concentration increases. The average CH_3OH concentration also rises as the light input and water vapor percentage increase, but declines with increasing the inlet velocity. The maximum conversion rate and quantum efficiency in the model are 0.235 μmol $g^{-1}h^{-1}$ and 0.0177% respectively, both higher than previous internally illuminated monolith reactor (0.16 μmol $g^{-1}h^{-1}$ and 0.012%). The optical fiber monolith reactor layout with multiple inverse lights is recommended in the design of photocatalytic reactor of CO_2 reduction.

1. Introduction

With global energy demand growing and fossil fuels consumption, the level of carbon dioxide (CO_2) in the atmosphere has been rising, which results in the greenhouse effect to cause environmental hazards [1–3]. In the past decades, the conversion of CO_2 to value-added chemicals and renewable fuels has been investigated by various methods such as thermal conversion, plasma conversion and photoreduction [4,5]. CO_2 reduction using solar light in a photocatalytic reactor is promising to relieve greenhouse effect and energy crisis [6]. In this way, solar energy can be converted and stored as chemical energy without producing greenhouse gases, similar to photosynthesis [7]. However, the conversion of CO_2 via H_2O splitting is relatively low [8], many studies focus on the field to improve the conversion, especially the efficient reactor design [9–12].

The photoreactor design is of great importance in the photocatalytic CO_2 reduction. Various reactors were summarized by Tahir and Amin [1,4], including optical fiber reactors [13–15], monolith reactors [16–18], slurry reactors [19], annular reactors [20], etc. Some of them are limited to the laboratory scale due to the layout of light resources and the long distance between the light and catalyst [17]. Comparatively speaking, optical fiber and monolith photoreactors are more efficient due to higher reaction surface area, efficient light harvesting, and uniform light distribution [1,9]. In order to further improve the illuminated surface area and light utilization, a distributive optical fiber monolith reactor (OFMR) was proposed by Lin and Valsaraj [21], which is made up of lots of parallel channels. On the condition that the variables such as flow flux and radiance flux are uniformly distributed at the monolith inlet and outlet, these reaction channels could be presumed identical [22]. The OFMR has some advantages over other reactors, first of which is that a honeycomb monolith substrate has 10–100 times greater specific surface area than that of other types of reactor substrates with the same external size [23]. Besides, the monolithic reactor is easy of scale and industrialization by increasing the number and dimension of channels, so the OFMR has been widely applied to the photocatalytic field.

However, the spectral range used in the CO_2 reduction is under 400 nm, only possessing nearly 3% of sunlight [24], so making full use of limited UV light attracts more attention in the photocatalytic research. Previous studies focused on selecting efficient catalyst and advanced methods, such as montmorillonite modified TiO_2 proposed by Tahir and Amin [9,25], and a simple method studied by Yang and Liu [26]. Except the synthesis of new catalysts and theoretical methods, lights layout is equally crucial to improve

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Nomenclature

C	concentration, mol m^{-3}
d	diameter, mm
D	diffusion coefficient, m^2 s^{-1}
f_θ	fraction of incident light with incident angle less than 90°
I	light intensity, W m^{-2}
k	kinetic rate constant, m^4 s^{-1} mol^{-2}
K	adsorption equilibrium constant
l	distance, mm
L	reactor length, mm
P	pressure, Pa
r	reaction rate, mol m^{-3} s^{-1}
R	radius, mm
s	distance, mm
T	temperature, K
u	velocity, m s^{-1}
V	molar volume, cm^3 mol^{-1}
z	axial position, cm

Greek letters

α	refractive loss coefficient, cm^{-1}
β	attenuation coefficient of the tip light flux, cm^{-1}
δ	catalyst film thickness, nm
ε	local attenuation coefficient of catalyst film, nm^{-1}
η	overall strengthened factor
θ	angle in Cartesian coordinates, rad
σ	fractional surface coverage
λ	overall factor
μ	molecular weight of gas
ν	viscosity, m^2 s^{-1}
ρ	density, kg m^{-3}
ϕ	quantum efficiency

Subscript and superscript

a	active sites
A	species
axial	axial
B	species
f	optical fiber
fc	fiber coating
inlet	inlet
input	input
m	monolith
mc	monolith coating
n	power law coefficient
outlet	outlet
output	output
s	surface
w	monolith channel wall
x	direction in Cartesian coordinates
y	direction in Cartesian coordinates
z	direction in Cartesian coordinates

the utilization ratio of energy input, but seldom taken into consideration.

In the present work, the model with four fibers inverse layout in a reaction unit was developed on the basis of OFMR. A new light distribution equation was derived using the geometrical methods. By means of the multiphysics software COMSOL, which has great advantages over the traditional physical experiments, the fiber location, inlet reactants velocity, reactants concentration and light input were investigated. This new optical fiber monolith reactor layout with multiple inverse lights can improve the conversion of CO_2 to CH_3OH and has a high quantum efficiency, which is of benefit to the design of the photocatalytic reactor of CO_2 reduction.

2. Computational models

In the simulated experiment, a complex integration of the submodels including the radiation field, the fluid dynamics, and the reaction kinetics is required to build the rigorous model. The model is involved in the modules of radio frequency, transport of diluted species and reaction engineering by the COMSOL software, whose biggest advantage is coupling multiphysics and submodels. With the assumption of all flow channels being identical, and the limited computing resources, a single unit of the honeycomb monolith with four inserted optical fibers is investigated as shown in Fig. 1. Comparing with previous research, the innovations of the present model lie in four fibers configuration in a reaction channel and light resources arranged in the products outlet. Besides the hypothesis that all channels are the same, each channel also takes the following assumptions:

(1) Gravity effect is ignored.
(2) The whole reaction channel is kept constant temperature with 298 K, in which the Arrhenius expressions can be neglected.
(3) All species are incompressible Newtonian fluid in steady flow conditions.
(4) The reaction area is fully developed laminar flow.
(5) Every channel is irradiated by four fibers arranged in the equal distance to the center of monolith. Moreover, the four optical fibers are uniformly distributed in the circumferential direction, which makes each fiber identical in the light transmission.
(6) The five reaction surfaces are uniform and fully covered by the TiO_2 catalyst with 1% $NiO/InTaO_4$(sg), whose physical properties are stable and never metamorphic.
(7) The photocatalytic reaction only occurs in the surfaces of four fibers and monolith wall with covered catalyst. The convection-diffusion of intermediates can be neglected.
(8) Light is absorbed by catalyst films only, neglecting the effects of the reactants and resultants.
(9) The following equation is used to characterize the overall photo reduction converting CO_2 to CH_3OH on the catalyst coating.

$$CO_2 + 2H_2O \xrightarrow[hv]{\text{catalyst}} CH_3OH + \frac{3}{2}O_2 \tag{1}$$

These simplifications mean that the reaction mechanism is ignored, and the conversion between the reactants and resultants is the key point of the simulation.

It is necessary in the numerical experiments that the above assumptions were proposed without producing large deviations.

2.1. Diffusion and reaction kinetics model

In a binary mixture of two gases A and B, the diffusion coefficient D can be obtained by the semi-empirical formula given by Gilliland [27]: