Sorption enhanced hydrogen production by steam methane reforming using Li$_2$ZrO$_3$ as sorbent: Sorption kinetics and reactor simulation

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Abstract

The kinetics of CO$_2$ sorption on a solid adsorbent, namely lithium zirconate, have been studied in an oscillating microbalance. The solid sorbent has been prepared by a novel route resulting in a high capacity, good stability and much improved sorption rates, making it suitable for its application in sorption enhanced hydrogen production by steam methane reforming. A kinetic equation for the sorption kinetics as a function of CO$_2$ partial pressure and temperature has been developed. The hydrogen production by sorption enhanced reaction process has been simulated by a dynamic one-dimensional pseudo-homogenous model of a fixed-bed reactor, where a hydrotalcite-derived Ni catalyst has been used as steam reforming catalysts. Simulation results show that hydrogen purer than 95% with a concentration of carbon monoxide lower than 0.2 mol% can be produced in a single step.
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Keywords: CO$_2$ sorption; H$_2$ production; Lithium zirconate; Enhanced steam reforming; Ni

1. Introduction

The issue of global warming is becoming a major element in the world energy policy. Presently, about 29 billion tonnes of CO$_2$ are released into the air annually by human activities, including 23 billion from fossil fuels burning and industry. According to the Kyoto protocol, this emission has to be dramatically reduced and it is then imperative to give high priority to the sequestration of CO$_2$ and efficient power generation [1].

Many studies have recently been carried out related to the CO$_2$ removal from flue gases. Currently available technologies for CO$_2$ separation include: physical and chemical absorption [2], physical and chemical adsorption [3], cryogenic processes and gas separation membranes [4]. Recently, special attention has been given to the use of lithium zirconate as CO$_2$ adsorbent at high temperatures [5–10]. Nakagawa and Ohashi [5,6] have reported that

lithium zirconate can theoretically adsorb CO$_2$ in amounts up to 28% adsorbent weight at high temperatures according to the following reaction:

$$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2; \quad \Delta H\,(298\,K)$$
$$= -160\,kJ/mol \tag{1}$$
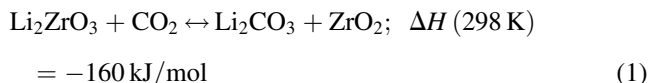
The high adsorption capacity and stability of this material make it increasingly promising for this purpose. However, kinetic limitations are still the main drawback.

The removal of CO$_2$ from hot gas streams is becoming very significant in the field of energy production. For example, the novel sorption enhanced reaction process (SERP) has the potential to decrease the cost of hydrogen production by steam methane reforming [11]. In this process, a CO$_2$ acceptor is installed together with the catalyst for removal of CO$_2$ from the gas phase and hence pushing the equilibrium limits for the reforming and water–gas shift reactions. It is possible to obtain a product containing as much as 97% H$_2$ (dry basis) [11]. The steam reforming can be run at much lower temperatures

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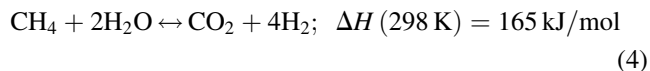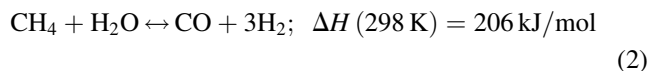E-mail address: chen@chemeng.ntnu.no (D. Chen).

Nomenclature

C	concentration (mol/m^3)
Cp_g	heat capacity of gas (J/mol K)
Cp_s	heat capacity of solid (J/mol K)
d_p	particle diameter (m)
d_t	internal reactor diameter
D_L	effective axial dispersion coefficient (m^2/s)
D_m	molecular diffusivity (m^2/s)
E_{ad}	energy of adsorption (J/mol)
ΔH_j	enthalpy of the reaction j (kJ/mol)
k_{ad}	rate constant for the adsorption
K_D	Ergun equation coefficient (N s/m^4)
K_V	Ergun equation coefficient (N s^2/m^5)
L	length of reactor (m)
M_i	molecular weight of i (g/mol)
n	exponent in the sorption kinetics equation
N_f	total reactor feed (mol/s)
P	total pressure in reactor (Pa)
P_{CO_2}	partial pressure of CO_2 (atm)
P_f	total pressure in reactor feed (Pa)
Pr	Prandtl's number
r_{ad}	sorption rate (mol/kg s)
R	gas constant (J/mol K)
R_i	catalytic reaction rate reaction i (mol/kg s)
Re_p	Reynolds number, based on particle
t	time (s)
T	temperature (K)
T_f	feed temperature (K)
T_w	wall temperature (K)
u	superficial gas velocity (m/s)
U	overall bed-wall heat transfer coefficient (J/ m^{2}K)
Δw	uptake of CO_2 (g CO_2/g absorbent)
x	extent of reaction
y_i	mole fractions of component i
y_{fi}	mole fractions of component i in feed
z	axial position (m)

Greek symbols

ε	void fraction in reactor
η_j	effectiveness factor of reaction j
λ_g	gas conductivity (W/mK)
λ_p	solid conductivity (W/mK)
λ_z	effective axial conductivity (W/mK)
μ	gas viscosity (Pa s)
ν_{ij}	stochiometric factor of component i in reaction j
ρ_b	density of the bed (adsorbent + catalyst) (kg/ m^3)
$\rho_{b,ad}$	bed density of adsorbent (kg/m^3)
$\rho_{b,cat}$	bed density of catalyst (kg/m^3)
ρ_g	density of gas (kg/m^3)

(723–903 K) than conventional steam reforming. As a result, investment and operation costs are significantly reduced. The key reactions of the process are the steam methane reforming (SMR) and the water–gas shift reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2; \quad \Delta H \,(298\,K) = 206\,kJ/mol \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2; \quad \Delta H \,(298\,K) = -41\,kJ/mol \tag{3}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2; \quad \Delta H \,(298\,K) = 165\,kJ/mol \tag{4}$$

In this work, we have used Li_2ZrO_3 to adsorb CO_2 during the reaction aiming to produce hydrogen with purity higher than 95%. The reported sorption rates of CO_2 on Li_2ZrO_3 are too low for enhanced steam reforming. However, a novel soft chemical method has recently been developed in our laboratory, which can significantly improve the CO_2 sorption kinetics of lithium zirconate. The present work deals with a kinetic study of CO_2 sorption using a tapered element oscillating microbalance (TEOM) [15]. The purpose has been to determine a kinetic equation for sorption of CO_2 and to use this kinetic equation in a fixed-bed reactor model in order to simulate the hydrogen production according to the SERP concept. A hydrotalcite derived Ni catalyst has been used as steam reforming catalyst [12].

2. Experimental

The solid sorbent, namely lithium zirconate, has been prepared by means of a novel soft chemical method in our laboratory [13]. The crystalline structure of the prepared sample was characterised by X-ray diffraction (XRD) analysis using Cu Kα radiation. The crystallite size was calculated using the Scherrer equation [14].

CO_2 sorption properties were evaluated using a tapered element oscillating microbalance [15]. The tapered element was loaded with 20 mg of Li_2ZrO_3 together with quartz particles. The samples were heated to 823–873 K with a heating rate of 10 K/min in pure Ar and kept for 60 min at atmospheric pressure. The CO_2 sorption was started by switching from Ar to a mixture of CO_2 and Ar while maintaining the temperature. The flow rates of Ar and the mixture were kept constant at 100 ml/min. After saturation of the adsorbent, the temperature was increased to 953 K and the flow gas was changed from CO_2/Ar mixture to Ar to proceed with the desorption reaction. The experiments were carried out at different CO_2 partial pressures and sorption temperatures. The different partial pressures of CO_2 were obtained by adjusting flow rates of CO_2 and Ar at a constant total flow rate of 100 ml/min.