



Applying spatially resolved concentration and temperature measurements in a catalytic plate reactor for the kinetic study of CO methanation

Jan Kopyscinski, Tilman J. Schildhauer*, Frédéric Vogel, Serge M.A. Biollaz, Alexander Wokaun

General Energy Research Department, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

ARTICLE INFO

Article history:

Received 19 November 2009

Revised 29 January 2010

Accepted 2 February 2010

Available online 31 March 2010

Keywords:

Kinetics

Catalytic plate reactor

Spatially resolved measurements

Methanation

Water gas shift reaction

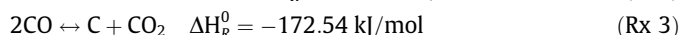
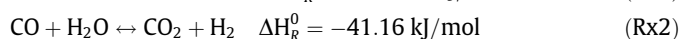
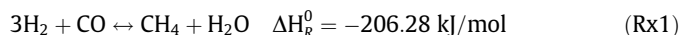
ABSTRACT

In this work, the successful application of spatially resolved measurements in an optically accessible catalytic plate reactor was demonstrated, which allows the detailed investigation of the reaction kinetics of the exothermic CO methanation reaction with high initial CO partial pressure. By means of a movable sampling capillary, the axial gas species concentration profiles over the catalyst plate were measured, and the catalyst surface temperature was determined simultaneously along the reactor through a quartz glass window by means of infrared thermography. A one-dimensional model of the catalytic plate reactor and a Bayesian approach were applied to estimate the kinetic model parameters of the proposed Langmuir–Hinshelwood rate expressions by comparing simulated and measured gas concentration profiles. The validity of using a computationally efficient one-dimensional model was proven by solving a two-dimensional model using the kinetic parameters determined with the one-dimensional model and by comparing the two results.

© 2010 Elsevier Inc. All rights reserved.

1. Introduction

Modeling and simulation of chemical reactors is advantageous as it allows to easily study the influence of the operation conditions on the reactor performance, while the experimental work is limited to validation experiments. A high quality of the model prediction can only be obtained if all relevant processes in a chemical reactor and their interactions are represented adequately. Besides hydrodynamics, heat and mass transfer, a proper description of the reaction kinetics is necessary. For strongly exothermic and fast reactions, the determination of accurate kinetic parameters can be a challenge, especially when these reactions are part of a reaction network. The complete hydrogenation of CO to methane, also known as methanation reaction, in the presence of higher CO concentrations is an example for such a system (Rx 1–3).



The methanation reaction, its thermodynamics, elementary mechanism, kinetics, and catalyst deactivation mechanisms have been investigated intensively since in 1902 Sabatier and Senderens [1] found that nickel and other metals (Ru, Rh, Pt, Fe, Co) catalyzed this reaction. Important findings are summarized in [2–7].

* Corresponding author.

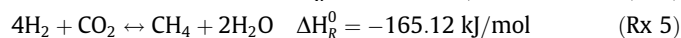
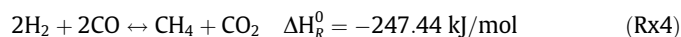
E-mail address: tilman.schildhauer@psi.ch (T.J. Schildhauer).

The heterogeneously catalyzed methanation is important in two main industrial applications: (1) removal of traces of CO in hydrogen-rich gases, i.e., for the ammonia synthesis and (2) conversion of synthesis gas to a methane-rich fuel with a high heating value, so called synthetic or substitute natural gas (SNG). In the latter case, the synthesis gas produced by the gasification of solid fuels may contain, besides high amounts of H₂ and CO, also CO₂, H₂O, CH₄, and higher hydrocarbons. Coal to SNG, developed in the 1960s to the mid 1980s, is an established industrial process, while recently a sustained effort has been made to convert biomass feedstock into SNG via biomass gasification followed by methanation of the synthesis gas [8].

Due to the high CO concentration, two other independent reactions (Rx 2) and (Rx 3) are important in the methanation of biomass-derived synthesis gas, besides reaction (Rx 1). If the stoichiometric ratio of the reactants H₂/CO is at least three or more, carbon monoxide reacts with hydrogen mainly to methane and water according to (Rx 1). However, producer gases from biomass gasifiers usually have an H₂/CO ratio between 0.3 and 2, which is too low for a high CO conversion and long catalyst lifetime. By means of the water gas shift reaction (WGS, (Rx 2)), the H₂/CO ratio can be adjusted by converting CO with H₂O to CO₂ and additional H₂. The Boudouard reaction (Rx 3) is of importance, since carbon on the catalyst surface can be considered as a necessary intermediate during the methanation reaction but can also lead to catalyst deactivation [9,10]. Methane can also be formed by hydrogenation of carbon oxides in two other reactions ((Rx 4) and (Rx 5)).

Nomenclature

a	specific surface area (m^{-2})	$\dot{n}_{b,i}$	molar flow of species i (mol s^{-1})
A	area (m^2)	p_i	partial pressure of species i (bar)
b	width of the catalyst plate (m)	\mathcal{R}	universal gas constant = 8.314 ($\text{J mol}^{-1} \text{K}^{-1}$)
$C_{b,i}$	bulk gas concentration of species i (mol m^{-3})	r_j	rate of reaction 1, 2 (methanation and water gas shift, respectively) ($\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1}$)
$C_{s,i}$	concentration on the catalyst surface of species i (mol m^{-3})	R_i	rate of disappearance or formation of species i ($\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1}$)
Ca	Carberry number (-)	Sh	Sherwood number (-)
D_{ij}	binary diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	T	temperature (K)
$D_{eff,i}$	effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	T_{ref}	reference temperature (598.15 K = 325 °C) (K)
$D_{i,mix}$	diffusion coefficient of species i in the gas mixture ($\text{m}^2 \text{s}^{-1}$)	u_{av}	average gas velocity (m s^{-1})
$D_{K,i}$	Knudsen diffusion coefficient of species i ($\text{m}^2 \text{s}^{-1}$)	$u_x(h)$	axial gas velocity at height h (m s^{-1})
Da_{II}	Damköhler number (-)	w_i	mass fraction of species i (-)
d_p	particle diameter (m)	x_i	molar fraction of species i (-)
d_{pore}	pore diameter (m)	Δx_i	interval width (-)
E_A	activation energy (kJ mol^{-1})	x, y	co-ordinates (m)
ΔH_i	adsorption enthalpy of species i (kJ mol^{-1})	Greek symbols	
$h(x_i)$	catalyst height in interval i (m)	ε	void fraction or porosity (-)
H	height of the channel (m)	η	catalyst effectiveness (-)
K_{Gi}	mass transfer coefficient of species i (m s^{-1})	ρ	density (kg m^{-3})
K_{eq}	equilibrium constant of the water gas shift reaction (-)	$\theta_{E,i}$	dimensionless activation energy (-)
K_i	adsorption constant of species i (differ)	$\theta_{H,i}$	dimensionless heat of adsorption (-)
K_i^0	pre-exponential factor of the adsorption constant K_i (differ)	ω_{cat}	catalyst length density ($\text{kg}_{\text{cat}} \text{m}^{-1}$)
k_j	rate constant of reaction j (differ)	Ψ	Weisz modulus (-)
k_j^0	pre-exponential factor for rate constant k_j (differ)	Φ	Thiele modulus (-)
l_{ch}	characteristic length (ratio of volume to surface) (m)	ϕ_p	particle sphericity (-)
M_{av}	molar mass of gas mixture (g mol^{-1})	τ	tortuosity (-)
M_i	molar mass of species i (g mol^{-1})	ν_{ij}	stoichiometric factor (-)
m	catalyst mass (kg_{cat})		



It has to be noticed that these reactions can be described as a linear combination of reactions (Rx 1) and (Rx 2). The CO_2 methanation (Rx 5) does not occur in the presence of CO [3], which could also be confirmed by experiments reported in this work (see Section 3.2).

In the past 50 years, more than 45 papers have been published regarding the kinetics of CO and CO_2 methanation, including the water gas shift reaction, over different nickel catalysts. However, in all of these studies only the gas composition at the reactor outlet for different experimental conditions was measured. By applying appropriate experimental conditions, the rate of the methanation reaction could be directly calculated from the conversion of CO or the exit gas concentration of CH_4 . Most of the investigators used a flow reactor with gas recycle (i.e., Berty type) [11–16] or without gas recycle [17–28] to collect the kinetic data. To avoid an excessive temperature increase due to the exothermic reaction, highly diluted gas mixtures (>90% inert gas), and diluted catalyst beds were used, or the reactor was operated as a differential reactor with a very low CO conversion [20,27]. The flow reactors contained catalyst amounts of a few hundred milligrams up to several grams with particle sizes from several μm [19,22] up to 6 mm [11]. In some cases, the length of the catalyst bed was varied [25]. The problem with highly diluted gas mixtures and low CO conversions is the necessity to precisely measure CO and CH_4 in the ppmv range. Klose [11] reported an analytical error of 7% for CO and CH_4 , and an even higher value for H_2 , N_2 , and CO_2 . Another serious limitation of these systems for kinetic studies is the necessity to reach a gas composition at the exit that is sufficiently far away from chemical equilibrium.

While these studies relied on measuring the exit gas composition only, gathering information on gas composition and temperature profiles along the reactor axis allows the investigation of the reaction kinetics in much more detail. Spatially resolved measurements of gas species concentrations have already been applied in several studies for the partial oxidation of methane on a rhodium-coated foam at high temperature [29–33] and for the low temperature autothermal reforming of methane and gasoline using an earlier version of the catalytic plate reactor in our laboratory [34,35]. Here, a movable sampling capillary was used to acquire data along the reactor. Another possibility is the non-intrusive measurement of the gas composition by applying Raman and Laser Induced Fluorescence (LIF) techniques [36] in an optically accessible reactor.

In this study, we demonstrate the successful application of spatially resolved measurements in a catalytic plate reactor to investigate the influence of different parameters on the methanation reaction. The kinetic parameters were determined by comparing measured gas species concentration profiles with those derived from a one-dimensional reactor model. The kinetics validated by means of the one-dimensional modeling were applied into a two-dimensional model to verify the underlying assumption that the influence of film diffusion is negligible under the studied experimental conditions.

2. Experimental

2.1. Test rig

A test rig for the determination of kinetic parameters in heterogeneously catalyzed reactions designed by Bosco [35] was used. For studying the methanation reaction in the parameter space of

Download English Version:

<https://daneshyari.com/en/article/61781>

Download Persian Version:

<https://daneshyari.com/article/61781>

[Daneshyari.com](https://daneshyari.com)