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Full Length Article

A study on three-phase CO_2 methanation reaction kinetics in a continuous stirred-tank slurry reactor

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ABSTRACT

The reaction kinetics of the three-phase CO_2 methanation for a commercial Ni/SiO_2 catalyst suspended in a liquid phase is studied in a continuous stirred-tank slurry reactor at a CO_2 partial pressure of 1 bar and temperatures from 220 °C to 320 °C. By applying different liquids, namely squalane, octadecane, and dibenzyltoluene, showing different gas solubilities, it is found that the gas concentration in the liquid phase and not the partial pressure in the gas phase is the driving force for the CO_2 methanation reaction kinetics. The liquid phase does not influence the reaction kinetics but reduces the available gas concentrations and H_2/CO_2 ratio on the catalyst surface. Based on these findings, a kinetic rate equation for the three-phase CO_2 methanation is developed additionally incorporating the chemical equilibrium limitations relevant in the temperature regime.

1. Introduction

With the COP21 Agreement, the parties of the United Nations Framework Convention on Climate Change agreed on reducing greenhouse gas emissions in order to keep the increase in global average temperature well below 2 K [1]. One way to achieve this goal is to reduce the CO_2 emissions through a drastic increase of the share of renewable and environmentally friendly energy sources like wind and sunlight in our energy systems. This electrical energy can be used to power many applications in the mobility and heat sectors. Nevertheless, the current share of electricity in final energy consumption is relatively low, e.g. about 22% in the EU [2]. To cover the rest of the energy demand would require a large extension of the existing renewable energy plants and power grid. One possible solution to tackle this issue is the application of Power-to-Gas (PtG) processes which aim at transforming renewable electrical energy into chemical energy carriers with high energy density which can be stored over long time periods. This is achieved through transforming electrical energy via water electrolysis into hydrogen which is subsequently transformed with carbon dioxide into methane in order to produce synthetic natural gas (SNG), see Eq. (1) [3–5]. At first glance, the transformation of hydrogen into methane seems an unnecessary step coupled with losses in overall efficiency. However, it offers many benefits, i.e. a very well developed infrastructure for transportation and storage and the use of SNG in a wide range of highly efficient final energy conversion technologies, e.g. decentralized/central combined heat and power units, mobility (compressed natural gas and liquefied natural gas) or combined cycle power plants [3,6,7].

$$CO_2(g) + 4H_2(g)CH_4(g) + 2H_2O(g) \quad \Delta h_R^0 = -165.1\ \text{kJ/mol} \tag{1}$$

The PtG process is a dynamic process allowing large-scale and flexible energy storage. Both electrolyzer and methanation reactor should be able to operate under dynamic conditions in order to limit the extent of expensive hydrogen storage technology. Considering the high exothermic methanation reaction (see Eq. (1)), heat removal from the reactor is one of the main issues related to the design of a methanation unit [8–10]. One way to tackle this issue is to run the methanation reaction in a slurry bubble column reactor, as this type of reactor allows for very efficient reactor temperature control as well as good dynamic behavior [11–14]. Slurry bubble column reactors are usually applied for Fischer-Tropsch synthesis, methanol and dimethyl ether production, hydrodesulfurization and hydrogenation of fatty oils as well as other hydrogenation and oxidation reactions [15–21].

Up to now, there is no reaction rate equation available in the literature for the reaction kinetics of the CO_2 methanation in a three-phase system. Especially the influence of the liquid phase on the reaction kinetics is not systematically investigated. Even looking at similar processes in the literature, the liquid-phase influence on reaction kinetics is still neither well-defined nor well understood. For the liquid-phase hydrogenation of cyclohexene on Pd, Madon et al. [22] showed that the H_2 concentration in the liquid phase is the determining factor to describe the reaction kinetics. However, when Pt is applied for the same reaction, Gonzo and Boudart [23] showed that the H_2 partial pressure in the gas phase is the determining factor. In three-phase

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Nomenclature

Symbols and abbreviations

A	Parameter describing the temperature dependency of CO_2 and H_2 Henry's law constant in DBT (see Eq. (4)) (–)
B	Parameter describing the temperature dependency of CO_2 and H_2 Henry's law constant in DBT (see Eq. (4)) (K)
C	Parameter describing the temperature dependency of CO_2 and H_2 Henry's law constant in DBT (see Eq. (4)) (K^2)
$c_{i,L}$	Concentration of gas component i in the liquid phase (mol/m^3)
$c^*_{i,L}$	Concentration of gas component i in the liquid phase at gas/liquid phase equilibrium (mol/m^3)
CSTR	Continuous Stirred-Tank Reactor (–)
DBT	Dibenzyltoluene (–)
Δh^0_R	Reaction enthalpy at standard conditions (J/mol)
E_A	Activation energy of the reaction (J/mol)
$H_{i,px}$	Henry's law constant of gas component i (see Eq. (2)) (bar)
$H_{i,pc}$	Concentration-based Henry's law constant of gas component i (see Eq. (3)) bar·(m^3/mol)
k	Reaction rate constant (see Eq. (10)) (mol/(kg·s·$mol^{0.4}$·$m^{-1.2}$))
k_0	Reaction rate constant in Arrhenius equation (mol/(kg·s·$mol^{0.4}$·$m^{-1.2}$))
K	Parameter to express the reaction rate limitation due to chemical equilibrium closeness (see Eq. (11)) (–)
K_{eq}	Equilibrium constant of the reaction (–)
K_{H_2O}	H_2O adsorption constant ($m^{0.3}/mol^{0.1}$)
m_{cat}	Catalyst mass (kg)
M_L	Liquid phase molar mass (kg/mol)
$\dot{n}$	Molar stream (mol/s)
p_0	Pressure at standard conditions (bar)
p_i	Partial pressure of gas component i (bar)
PtG	Power-to-Gas (–)
r_{3PM}	Catalyst mass-specific CO_2 reaction rate (mol/(kg·s))
R	Ideal gas constant (J/(mol·K))
SNG	Synthetic Natural Gas (–)
T	Temperature (°C or K)
x_i	Molar fraction of gas component i in the liquid phase (–)
X_{CO_2}	CO_2 conversion (see Eq. (6)) (–)
y_i	Molar fraction of gas component i (–)
α	H_2 reaction order (–)
β	CO_2 reaction order (–)
γ	H_2O reaction order (–)
ρ_L	Liquid phase density (kg/m^3)
τ_{mod,CO_2}	Modified CO_2 residence time (see Eq. (7)) (kg·s/mol)
3PM	Three-phase methanation (–)

Subscripts and superscripts

cal	Calculated
cat	Catalyst
exp	Experimental
G	Gas phase
i	Gas component i
in	Reactor inlet
L	Liquid phase
out	Reactor outlet

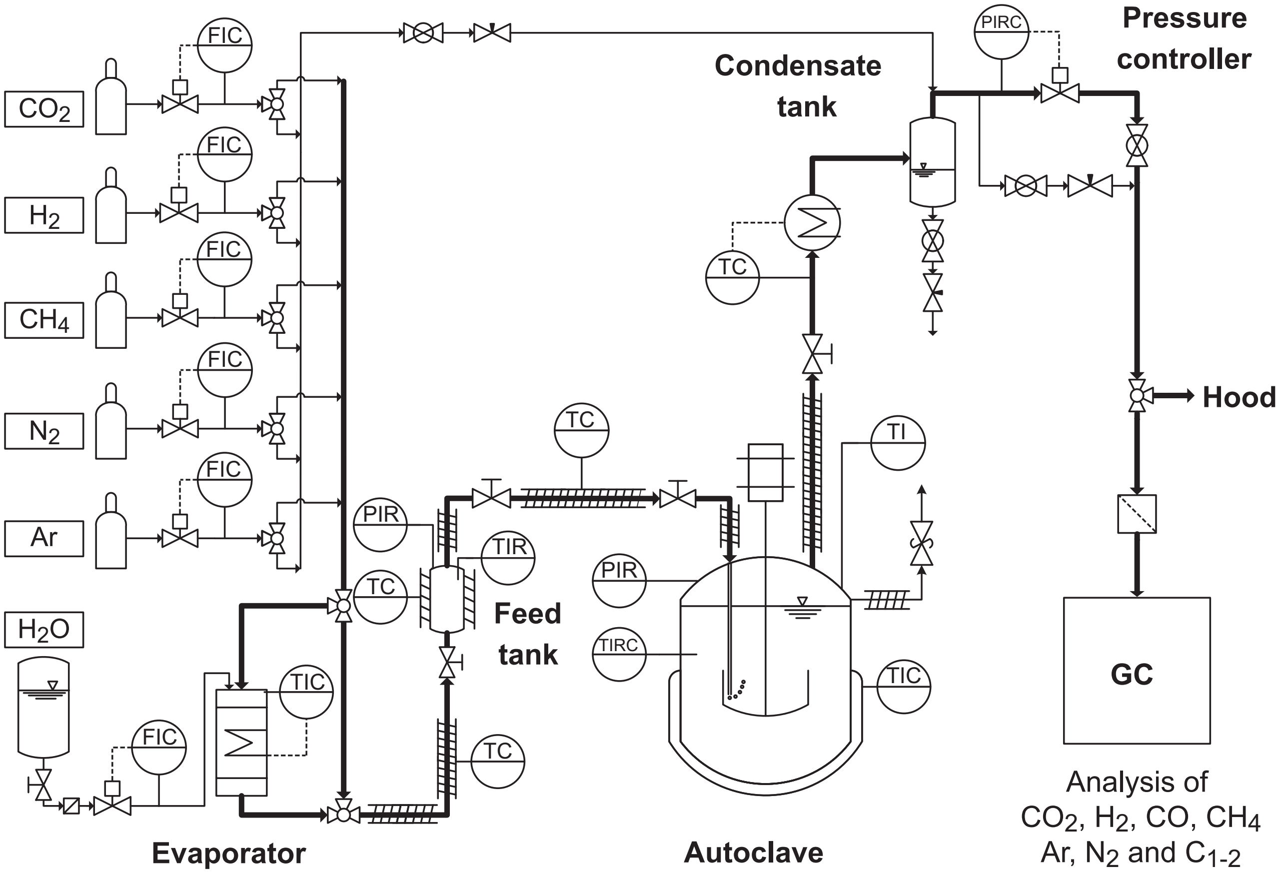

Fig. 1. Flow scheme of the experimental setup.