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Interplay of reaction and pore diffusion during cobalt-catalyzed Fischer–Tropsch synthesis with CO₂-rich syngas

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ABSTRACT

For cobalt-catalyzed Fischer–Tropsch synthesis (FTS), a model was developed to analyze numerically the reaction–diffusion performance in catalyst particles. The model is based on a mesoporous particle and is valid for CO₂-free and -rich syngas. The kinetic parameters of all three relevant reactions, CO hydrogenation to C₂₊ hydrocarbons as well as CH₄ and CO₂ hydrogenation (mainly) to CH₄, were derived at intrinsic conditions ($d_p = 150 \mu\text{m}$). Thereafter, the effective kinetics considering pore diffusion limitations were derived by using a homemade catalyst in 5 mm diameter. From the data measured, a kinetic approach for conversion of CO₂ inside the catalyst particle was developed. The experimentally derived Langmuir–Hinshelwood type rate expressions and a variable chain growth parameter α , dependent on temperature and syngas ratio, were implemented into the model. Furthermore, the change of the local reaction rates and selectivities, as a consequence of changing syngas ratio due to diffusion limitation is taken into account. The simulated data of effective kinetics and selectivities are in agreement with the measured data. The simulation predicts that CO₂ is only converted in the CO-free core region of large catalyst particles at high temperatures and strong pore diffusion limitations. For CO₂ converts mainly to CH₄ (selectivity 95%_C), a slightly increased overall methane selectivity is expected indicating consumption of CO₂. However, this effect was not measurable even with 5 mm particles at high temperatures as methanation of CO₂ occurs only to a minor extent even at pronounced diffusion limited conditions and is negligible at industrial conditions.

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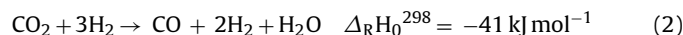
1. Introduction

The Fischer–Tropsch synthesis (FTS) is an attractive way to convert syngas (today based on natural gas, coal, heavy oil or biomass) into highly valuable hydrocarbon products like jet fuel, diesel oil and petrochemicals (see Eq. (1), where $-(\text{CH}_2)-$ represents a methylene group of normal paraffin) [1,2].



FTS is currently also discussed as an option to utilize CO₂ (e.g. separated from flue gases of fossil fuel based power plants) and (renewable) hydrogen from water–electrolysis for fuel production;

in this case, syngas (CO) is produced via reverse water–gas shift (see Eq. (2)) [3–6].



Under typical low-temperature FT conditions (LT-FT) (220 °C, 3 MPa), cobalt as active metal yields predominantly longer-chain paraffinic hydrocarbons (diesel oil, jet fuel and waxes); the waxes may be hydrocracked downstream to enhance the overall yield of valuable liquid fuels [6–9]. Beside slurry phase reactors, multi-tubular fixed bed reactors are common in industrial application [10–12]. However, these reactors tend to exhibit a significant pressure drop [12]. Hence, catalyst dimensions of several millimeters (1–3 mm) are to be chosen [13]. Thus, internal transport limitation occurs having an impact on the effective reaction rate as expressed by the effectiveness factor η [14–17]. The Thiele modulus ϕ characterizes the influence of diffusion on the kinetics of heterogeneously catalyzed reactions since ϕ defines the interplay between reaction rate r_i in a porous particle and mass transport by pore diffusion [18–20]. For Thiele modulus analysis, the literature provides expressions based on simplified kinetics (mostly first order in H₂ or CO) to describe the effective kinetics approximately

Abbreviations: BET, Brunauer, Emmett and Teller: surface analysis method; BJH, Barrett, Joyner and Halenda: pore size distribution determination method; EDX, energy dispersive X-ray spectroscopy; FTS, Fischer–Tropsch synthesis; LH, Langmuir–Hinshelwood; LT-FT, low-temperature Fischer–Tropsch synthesis; PTL, power-to-liquid; TG, thermogravimetry.

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[21–23]. However, these approaches have their limits; a lot of simplifications have to be made especially with regard to the intrinsic kinetics, gas–liquid equilibria and mass transport by diffusion. For example, with respect to Thiele moduli analysis, only the kinetics of CO consumption and the effective diffusivity of CO are usually taken into account, whereas concentrations of other species are considered as constant [5,24]. These approximations are inappropriate to predict accurately the influence of mass transport on local reaction rates as well as on selectivity.

Therefore, numerical analysis is the preferential mathematical method applied to describe the reaction–diffusion performance of FTS in a catalyst particle precisely. Here, the analysis of the diffusivity and solubility of the reactants in the liquid hydrocarbons inside the catalyst's pores, which are filled with liquid higher hydrocarbons (waxes) during LT-FTS, is essential. The solubility of CO is 1.3 times compared to the H₂-solubility [25–29]. Hence, a stoichiometric H₂-to-CO (syngas) ratio in the gas phase of 2 yields a ratio of about 1.6 in the liquid phase, at least for the concentrations at the external surface of the particle ($c_{i,liq,S}$), i.e. at the pore mouth [14]. The diffusion coefficient of H₂ (in higher liquid hydrocarbons) exceeds the one of CO by a factor of 2.7 [16]. Consequently, the absolute value of the gradient of the concentration of H₂ in the particle ($dc_{H_2,liq}/dr$) is lower compared to CO, even if we consider the stoichiometric H₂-to-CO consumption ratio of 2 ($dc_{H_2,liq}/dr = 2/2.7 \cdot dc_{CO,liq}/dr = 0.74dc_{CO}/dr$). For illustration: in case of strong limitation by pore diffusion, the concentration of CO in the liquid phase ($c_{CO,liq}$) reaches almost a value of zero in the core region of the particle, whereas H₂ is still present; for the given example ($c_{H_2,liq,S} = 1.6 \cdot c_{CO,liq,S}$), the residual value of $c_{H_2,liq}$ in the CO-free core region would be still about $0.9c_{CO,liq,S}$ ($= (1.6 - 0.74) \cdot c_{CO,liq,S}$) and $0.5c_{H_2,liq,S}$, respectively.

A numerical study of reaction and diffusion in a FTS catalyst (Co or Fe) in itself is not new. In the literature, several studies report the performance of catalyst particles [14,16,17,30,31]. However, the majority of these studies omit that the rates and selectivities inside the catalyst particle may change because of locally shifting syngas ratios. Furthermore, syngas produced from natural gas, coal or biomass contains significant amounts of carbon dioxide [32]. However, none of the models deals with the fate of CO₂; to put it in another way, whether CO₂ behaves as an active carbon source for FTS with cobalt as catalyst or acts only as an inert during the process [5,33–35].

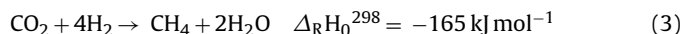
In this study, the focus is on the simulation of concentration, reaction rate and selectivity profiles inside a catalyst particle at variable operating parameters (i.e. temperature, syngas ratio) using CO₂-free and CO₂-rich syngas in order to fit our experimental data at effective conditions best. These experiments should provide clarity about the question whether CO₂ converts to hydrocarbons at severely diffusion limited conditions in the possibly CO-free core region of the catalyst pellet or still behaves as an inert only.

At first, extensive intrinsic experiments were conducted to validate the Langmuir–Hinshelwood mechanism and determine rate expressions for the methanation, the production of liquid hydrocarbons and the consumption of CO and CO₂. A variable model of the chain growth probability derived by Vervloet et al. was implemented to describe the local selectivity to long-chain hydrocarbons as a function of temperature and syngas ratio. Under typical LT-FT conditions, concentration gradients of the syngas species are expected inside the catalyst due to mass transport limitation, leading to an increasing H₂-to-CO ratio toward the center of the catalyst particle [14]. Thus, if this phenomenon comes up, an impact on the catalyst performance in terms of reaction rate and selectivity is about to happen. At severely diffusion limitation (i.e. high temperatures and large particles), almost complete conversion of CO inside the catalyst can occur. For CO is not available anymore, CO₂ can

Table 1
Characteristic data of the cylindrical cobalt catalyst.

Parameter	Value
Geometric dimension ($l_p \times d_p$)	5 mm × 5 mm
Cobalt content	10 wt.%
Platinum content	0.03 wt.%
BET surface area	180 m ² g _{cat} ⁻¹
Cumulative pore volume	0.34 cm ³ g _{cat} ⁻¹
Mean pore diameter	7 nm
Porosity	0.53
Apparent density	1600 kg m ⁻³
Crushed particles (d_p)	<150 μm

now adsorb on the active cobalt sides and is hydrogenated mainly to methane [5,33,35–40]:



2. Materials and methods

The experiments were carried out in a continuous flow apparatus under typical low-temperature Fischer–Tropsch conditions (190–260 °C, 3 MPa). The flow rates of synthesis and diluting gases (CO, CO₂, H₂, N₂) are varied by mass flow controllers (Brooks Instruments). The lab-scale FT reactor consisted of a single stainless steel tube (inner diameter: 14 mm) clad with an aluminum cylinder (diameter: 180 mm) to ensure isothermal conditions along the fixed bed. An electrical heating jacket adjusted the operating temperature, which was controlled by a movable thermocouple. Total pressure was regulated via a backpressure valve. To separate the waxy HC fraction, the product stream passed through a pressurized hot wax trap at 120 °C as well as additional cooling traps at ambient pressure (room temperature, 0 °C). The gaseous hydrocarbons (C₁–C₆) were analyzed online by GC (Varian 450-GC) using cyclopropane as internal standard; the 1% cyclopropane/N₂ mixture was added to the product stream before entering the GC. The chain growth probability α was correlated with the selectivity to long-chain hydrocarbons, namely the C₅₊-selectivity, from the gas phase. Further details of this method are presented in [41]. The concentration of CO, CO₂ and CH₄ was detected by online gas analysis via infrared absorption and the H₂ concentration was recorded with a thermal conductivity sensor (Fisher-Rosemount NGA 2000).

The homemade cobalt catalyst was used in the experiments; cobalt was deposited via wet-impregnation. The cylindrical particles (5 mm × 5 mm) were made of γ -Al₂O₃ as support material (purchased from SASOL). The support was stirred in an aqueous solution of cobaltous nitrate hexahydrate and tetraamineplatinum(II) nitrate (900 ml H₂O, 1 kg Co(NO₃)₂·6H₂O, 2 g Pt(NH₃)₄(NO₃)₂). The pellets were impregnated in 100 g scale in a round-bottomed flask. The flask was rotated under reduced pressure (30 kPa) at 40 °C on a rotavap apparatus in order to guarantee homogeneous cobalt dispersion during the slow evaporation of the solvent. EDX-measurements showed that cobalt and thus the catalytic active sites are dispersed homogeneously over the entire particle (see [42]). The solid was dried at room temperature and calcined in an air stream at 360 °C for 3 h. A summary of all catalyst characteristics is presented in Table 1. For experiments at intrinsic conditions, the catalyst particles were crushed ($d_p < 150 \mu\text{m}$) to minimize diffusion paths. For experiments at diffusion limited conditions, cylindrical catalyst particles of 5 mm in length and diameter were used. This very large catalyst dimension of 5 mm was chosen in order to realize strong effects of pore diffusion on catalyst effectiveness and product selectivity for a better scientific understanding. Hence, note that at industrial conditions ($d_p = 1\text{--}3 \text{ mm}$, $T = 200\text{--}240 \text{ °C}$) these severely diffusion limited conditions ($d_p > 3 \text{ mm}$, $T > 250 \text{ °C}$) are never achieved and such strong effects on reaction rates and selectivity as presented

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