

Research article

Performance of supported and unsupported Fe and Co catalysts for the direct synthesis of light alkenes from synthesis gas

Jens Schneider^{a,*}, Marlen Struve^a, Ulf Trommler^b, Michael Schlüter^a, Lisa Seidel^a, Sebastian Dietrich^a, Stefan Rönsch^{a,c}^a Syngas Technologies, DBFZ Deutsches Biomasseforschungszentrum Gemeinnützige GmbH (the German Centre for Biomass Research), Torgauer Str. 116, 04347 Leipzig, Germany^b Department of Environmental Engineering, Helmholtz Centre for Environmental Research – UFZ, Permoserstr. 15, 04318 Leipzig, Germany^c Department of Industrial Engineering, Ernst-Abbe-Hochschule Jena, Carl-Zeiss-Promenade 2, 07745 Jena, Germany

ARTICLE INFO

Keywords:

Synthesis
Ethene
Propene
Fischer-Tropsch
Olefins
Syngas

ABSTRACT

A sustainable way to produce plastics made from biomass (biomass to gas) and electricity (power to gas) could be obtained by the direct synthesis of light alkenes. Samples (≤ 1 g) of the bulk catalysts Co/Fe, Fe/Na/S and the supported catalysts Fe/Mn|MgO and Co|SiO₂ are mentioned in the literature to allow the direct synthesis of light alkenes. These materials are studied in extended fixed beds with catalyst amounts between 35 and 70 g and classic syngas (H₂ and CO) in this work in order to prepare a potential scale-up of this technology.

The influence of activation conditions (H₂ or CO as reduction agent; 350 or 420 °C at 1.5 bar) and synthesis temperature (230–500 °C) on catalyst activity and product selectivity are pointed out. Selectivities to ethene of up to 11% are found for Fe/Mn|MgO at $T \approx 440$ °C and for Fe/Na/S at $T \approx 310$ °C. The other materials did not produce significant amounts of ethene. CO₂ and CH₄ were the main products in any case, while C₂H₆ was the main C₂ product. Applying CO as reduction agent was superior to activation with H₂ at low times on stream (< 20 h). This is justified by the fast formation of carbides with CO as reduction agent since they are the most catalytically active species on Fe catalysts. The low selectivities observed for ethene are likely caused by the low GHSV value of 160 h⁻¹ applied in this study, which facilitates the conversion of primary alkenes in secondary reactions. Recommendations on operational conditions of Fischer-Tropsch to olefins processes are specified.

1. Introduction

1.1. Background

Iron and cobalt catalysts are applied in several commercial Fischer-Tropsch plants in South Africa, the Middle East and China that convert coal and natural gas in different reactor concepts [1,2]. The low-temperature approach (200–240 °C) targets at waxes as main products, whereas the high-temperature approach (300–350 °C) favors the formation of gasoline and diesel [3,4].

Besides these target products, light alkenes are of interest since they represent high-value bulk commodities with increasing demand of the plastic and chemical industry [5]. Light alkenes like ethene and propene show the highest production amounts of all organic chemicals [5]. More than half of the global plastic production capacity of about 300 million tons per year is based on these monomers [6]. But only below 1% of the raw materials used for recent global plastic production originate from biomass [6,7].

The direct synthesis of light alkenes (Fischer-Tropsch to olefins) represents a process, which has not been commercialized yet and can produce light alkenes explicitly from biomass. Thermo-chemical pre-treatments, e.g. pyrolysis and gasification, are necessary for syngas provision. Besides that, methanol to alkenes synthesis, Fischer-Tropsch synthesis including cracking of Fischer-Tropsch products and oxidative coupling of methane [8–11] are commercialized processes, which target at the production of light alkenes but start with coal or natural gas as feedstock.

A principle process scheme is demonstrated in Fig. 1. Excess electricity can be exploited by water electrolysis for hydrogen provision, which is especially needed for the fermentation path. Separation of alkenes and alkanes might be conducted by pressure swing adsorption with silver zeolite A [12] or silver nitrate dispersed on aluminosilica or clay [13].

In order to facilitate the application of new catalysts in pilot scale, studies of catalysts in microreactors [14] or small fixed beds with catalyst amounts of 1 g and below are the first step. Process conditions like

* Corresponding author.

E-mail address: Jens.Schneider@dbfz.de (J. Schneider).<https://doi.org/10.1016/j.fuproc.2017.10.018>Received 28 July 2017; Received in revised form 25 October 2017; Accepted 27 October 2017
0378-3820/ © 2017 Elsevier B.V. All rights reserved.

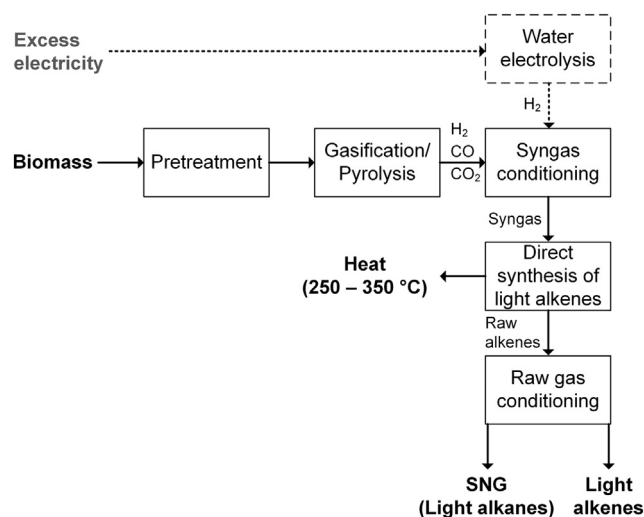


Fig. 1. Simplified process scheme for the conversion of biomass into light alkenes with SNG as byproduct. Hydrogen provision, e.g. by water electrolysis, is optional.

catalyst temperature and gas composition can be set easily in such setups. In contrast, fixed beds of decimeter and larger sizes are characterized by distinct gradients of temperature and gas composition since these quantities change steadily along the direction of gas flow. Problems like hot spots, reactor blocking due to coke formation and altered gas compositions due to undesired reactions of the product gas with the catalyst at the bottom end of a fixed bed are rarely taken into account in studies with very low catalyst amounts.

1.2. Aim of this study

It is the goal of this work to point out the influence of activation and process conditions on CO conversion and product selectivities for different Fe and Co test materials in an extended fixed bed. Promising combinations of catalyst and process conditions are expected from that.

A 41 cm long fixed-bed reactor with ten internal thermocouples and external heating is applied for synthesis studies. Between 35 and 70 g of catalyst are placed in this reactor with a distinct temperature profile. Different catalytically active materials are provided by an industrial catalyst manufacturer. The calcined catalysts are studied regarding their CO hydrogenation and alkene synthesis abilities at 230–500 °C, 1.4–2 bar, H₂/CO ratios of 3 and 1, and gas hourly space velocity (GHSV) = 160 h⁻¹.

A background on the direct synthesis of light alkenes is given in Section 2. Experimental conditions applied and the procedure for data evaluation is presented in Sections 3 and 4. Results and a discussion of them are given in Sections 5 and 6. Summary and conclusions follow in Section 7.

2. Background on the direct synthesis of light alkenes

2.1. Basic process conditions

This process receives increased attention since the 1980's and could accelerate the still slow substitution of fossil-based plastics by biomass-based. Torres Galvis and de Jong published a review about catalysts for the direct thermo-chemical production of light alkenes from synthesis gas in 2013 [11]. Results about many supported and unsupported catalysts, of which most are on the basis of iron and/or cobalt, are summarized by them. Temperatures and pressures studied by most authors vary between 250 and 450 °C and 1–25 bar at H₂/CO ratios of 1–3. At these conditions, maximum selectivities to C₂–C₄ alkenes are expected, while methane, carbon dioxide, and water represent major byproducts [11]. Lower amounts of C₂–C₄ alkanes, C₅ + hydrocarbons as well as

oxygenated hydrocarbons are produced additionally. Zohdi-Fasaee et al. found optimal conditions for light alkene synthesis at 312 °C, 2 bar, H₂/CO = 1 and GHSV = 4500 h⁻¹ with a Co/Mn/Ce|SiO₂ catalyst [15].

Several studies have shown that the activation conditions like reduction agent (H₂, CO or H₂ and CO) and temperature have major influence on catalyst activity and selectivity to light alkenes with Fe [16–19]. This is mostly attributed to the formation of different iron carbides like ε'-Fe_{2.2}C, χ-Fe_{2.5}C, and θ-Fe₃C, which are the active phases responsible for the formation of hydrocarbon products with two or more carbon atoms and can convert into each other under certain conditions [16–20].

Beside the process conditions, the catalyst applied plays a major role. Unsupported or bulk catalysts for the direct synthesis of light alkenes show a low mechanical stability due to carbon deposition or density differences between oxidic and carbidic phases [11,19,21]. These problems might be overcome by reducing the size of the active material to the range of nanometers, which can be induced with the help of a supporting material. Agglomeration of particles of the active material is reduced in this way, so that the formation of carbon depositions and the fragmentation of individual catalyst particles is reduced or inhibited [11,22].

From the list of catalysts reviewed by Torres Galvis and de Jong [11], two supported and two unsupported examples, which showed high alkene selectivities at high CO conversions, are selected and studied in this work. The results of these studies in small reactors are presented in the following.

2.2. Selected studies with bulk and supported catalysts

2.2.1. Co/Fe bulk catalyst

Mirzaei et al. prepared and studied an unsupported catalyst that contained ca. 47 wt% cobalt, 28 wt% iron, 4 wt% silicon and 21 wt% oxygen with small amounts of potassium [23]. It is made by co-precipitation of aqueous solutions of the hydrates of cobalt and iron nitrate, silica powder and potassium nitrate. Synthesis experiments are performed with 1 g of meshed material in a fixed-bed reactor at 1 bar, temperatures between 350 and 500 °C, H₂/CO ratios of 1–4, and GHSV of 4050–5400 h⁻¹. CO conversions are > 80% with C₂H₄ selectivities between 8% (H₂/CO = 1) and 30% (H₂/CO = 4) as well as C₃H₆ selectivities between 26% (H₂/CO = 1) and 23% (H₂/CO = 4) [23]. Other products like CH₄, H₂O, CO₂ seem to have not been taken into account, which explains the extraordinarily high selectivities mentioned. It was reported that the Co/Fe catalyst kept its activity and selectivity in a 72 h test at the best operation conditions (450 °C, H₂/CO = 4, GHSV = 5400 h⁻¹) [23].

2.2.2. Fe/Na/S bulk catalyst

Botes et al. modified an iron catalyst of Sasol promoted with sodium and sulphur that showed a high affinity for C₂–C₄ products (mainly alkenes) and a low methane selectivity (< 15%) at a CO conversion to hydrocarbons of 40% [24]. Five non-metal promoters namely boron, phosphorous, sulphur, chlorine and antimony are combined with sodium or potassium. Amounts between 0.4 and 5 mmol of non-metal promoters and between 1.6 and 25 mmol of alkali promoters are added to 1.78 mol (100 g) of iron in the form of iron(III) nitrate. In total, 306 catalysts are prepared and tested in an Avantium Nanoflow catalyst testing unit. 15 catalysts with sizes of 38–150 μm (25 mg) are tested in parallel. The catalysts are activated with H₂ at 420 °C and 20 bar for 16 h. Hydrocarbon synthesis conditions are set to 330 °C, 20 bar, educt gas composition of 57 vol% H₂, 14 vol% CO and 11 vol% CO₂ with He in balance and a flow rate of 12.9 L (g h)⁻¹ (NTP) [24]. The latter approximates a GHSV of 320 h⁻¹. Synthesis products are measured by gas chromatography with thermal conductivity detector (GC-TCD), GC with flame ionization detector (GC-FID) and GC with mass spectrometry (GC-MS). The combination of sodium and sulphur yielded the highest selectivities to C₂–C₄ alkenes with low methane selectivities

Download English Version:

<https://daneshyari.com/en/article/6656544>

Download Persian Version:

<https://daneshyari.com/article/6656544>

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