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## Enhanced olefin production in Fischer–Tropsch synthesis using ammonia containing synthesis gas feeds

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### ABSTRACT

The impact of ammonia in Fischer–Tropsch synthesis was studied using iron- and cobalt-based catalysts. Ammonia was co-fed to the synthesis gas feed with ammonia concentrations varying between 0 and 26 vol%. During conventional Fischer–Tropsch experiments the formation of paraffins,  $\alpha$ -olefins, alcohols and carboxylic acids was observed. Upon ammonia addition, the selectivity to  $\alpha$ -olefins could be significantly increased at all levels of ammonia addition. The conversion of CO was only affected slightly for low NH<sub>3</sub> contents, but decreased rapidly at high NH<sub>3</sub> concentrations in the synthesis gas feed. The formation of oxygenated products was suppressed in the presence of ammonia and the formation of nitrogen-containing compounds such as amines and amides was observed, suggesting a reaction of ammonia with oxygen containing compounds or surface intermediates.

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### 1. Introduction

The Fischer–Tropsch synthesis (FTS) is a polymerization reaction of monomers generated from carbon monoxide (CO) and hydrogen (H<sub>2</sub>) to generate a wide variety of products such as paraffins, olefins and oxygenated compounds including aldehydes, alcohols, ketones and carboxylic acids [1]. In general, the reaction takes place on transition metal catalysts (iron, cobalt) at moderate to high pressures and elevated temperatures. The products obtained from Fischer–Tropsch processes are sold as fuel, gasoline, jet fuel or diesel, but the Fischer–Tropsch process also produces more valuable chemicals, such as olefins and alcohols, which can be marketed as speciality chemicals [1]. Olefins are of great interest since they sell at much higher prices than fuels. They can be used as feedstock for the production of polyethylene or polyvinylchloride (ethylene) and polypropylene or acrylonitrile (propylene). Long chain olefins are widely used as co-monomers (C<sub>6</sub>–C<sub>8</sub>) in polyethylene production. Furthermore, higher olefins can be converted into valuable alcohols via hydroformylation [1]. Linear  $\alpha$ -olefins are thought to be the main primary products in the Fischer–Tropsch synthesis [2]. They are however rather reactive and can re-adsorb on the catalyst surface undergoing secondary reactions such as iso-

merization (double bond shift), hydrogenation to corresponding paraffins or re-insertion to act as chain starters (Fig. 1). Hence, the selectivity to olefins or other FT products is controlled to a large extent via the reaction conditions such as temperature, pressure, reactor design or catalytic metal. In this context, high-temperature fluidized-bed Fischer–Tropsch reactors with iron catalysts are ideal for the production of large amounts of linear olefins as conducted in on a large scale by Sasol in South Africa [1].

It has been reported [3,4] that co-feeding of ammonia to the synthesis gas feed under FT conditions can influence the FT product distribution significantly. In general, in small concentrations (ppm levels) ammonia is known to poison transition metal catalysts, which can cause deactivation and loss of catalytic activity [3,5,6]. Despite this fact, it has been reported that small amounts of NH<sub>3</sub> (10 ppm) in the synthesis gas feed can also slightly increase olefin/paraffin ratios during Fischer–Tropsch synthesis [3]. A significant increase in the olefin content from 54 to 67 wt% was observed in iron-based Fischer–Tropsch synthesis upon the addition of 20 vol% of ammonia in a slurry reactor [4]. The conversion of CO decreased only slightly in the presence of ammonia and no changes in methane selectivity or chain growth probability were observed [4]. Besides beneficial effects of NH<sub>3</sub> on olefin selectivity it is feasible to extend the wide FT product spectra by other valuable products upon ammonia addition. Several publications report about the formation of nitrogen-containing compounds such

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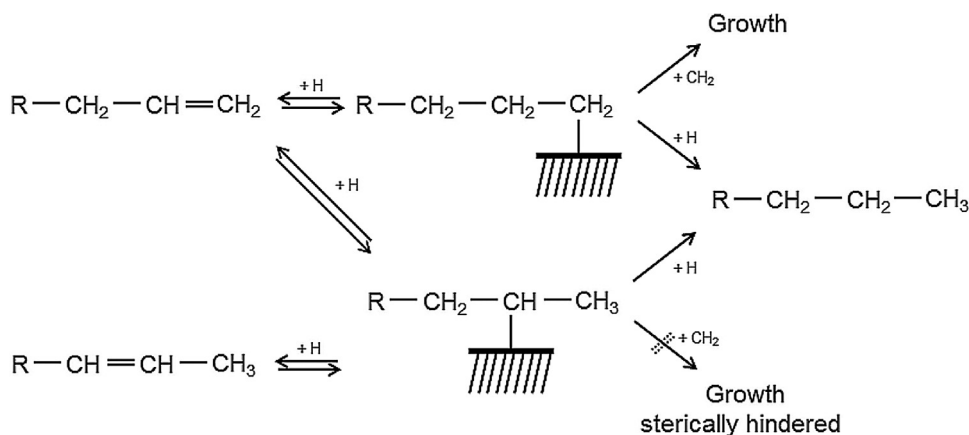


Fig. 1. Secondary reactions of linear  $\alpha$ -olefins after re-adsorption onto the catalyst surface.

(Adapted from [2])

as nitriles [4,8–10,13,16,17] amines [7,11,12,14,15,17] or amides [4,17].

This article will give further insight in product selectivity obtained from the Fischer–Tropsch synthesis using supported iron and cobalt-catalysts when ammonia is present in the synthesis gas feed at higher concentrations.

## 2. Experimental

### 2.1. Catalyst preparation

Cobalt and iron containing catalysts with different metal contents were prepared for the catalytic experiments. For all catalysts,  $\text{SiO}_2$  (Sigma–Aldrich Davisil 646, surface =  $110 \text{ m}^2/\text{g}$ , pore volume =  $0.3 \text{ mL/g}$ ) was used as support. This type of support was chosen so that a reasonable degree of reduction could be attained without the addition of a reduction promoter, which may have increased the level of complexity in the interpretation of the results. Furthermore, Sewell et al. [18] showed that the use of a non-acidic support results in a larger metal surface area.

A metal loading of 30 wt% was achieved via precipitation from a hot aqueous solution of cobalt nitrate solution (Riedel-de Haën). Under constant stirring, a hot ammonia hydroxide solution (5 wt%) was added until pH 7.5 followed by the addition of  $\text{SiO}_2$ . The catalyst precursor was filtered off, washed with hot deionized water and dried over night at  $130^\circ\text{C}$  in an oven.

Cobalt and iron catalysts with 15 wt% Co or Fe on  $\text{SiO}_2$  were synthesized by means of wet impregnation. A suspension of cobalt nitrate and iron nitrate (Riedel-de Haën), respectively, water and  $\text{SiO}_2$  was stirred for 5 h at room temperature and dried at  $110^\circ\text{C}$  for 16 h.

### 2.2. Fischer–Tropsch experiments in a slurry reactor

The 30 wt% Co/ $\text{SiO}_2$  catalyst was used for the FT experiments in a slurry reactor, which is described in [2]. Prior to the Fischer–Tropsch synthesis experiments, 11 g of catalyst was reduced in a fluidized bed reactor in 60 mL/min hydrogen at  $430^\circ\text{C}$  for 16 h. The reduced catalyst was transferred, under argon atmosphere, into molten wax to prevent the metallic cobalt from oxidizing and then, again under inert atmosphere, transferred into a 600 mL stainless steel vessel which was loaded with 250 g of molten wax. The reactor was purged in argon, pressurized to 12 bar and the temperature was set to  $240^\circ\text{C}$ . A total synthesis gas flow rate of 150 mL/min ( $\text{H}_2:\text{CO}$  ratio = 2) for FT experiments in the absence of ammonia was applied. A mixture of cyclohexane in

argon (0.15 mol%) was used as internal standard. In order to study the effects of different ammonia concentrations on CO conversion and product selectivity, the ammonia content in the synthesis gas feed was varied (0–26 vol%  $\text{NH}_3$ , Table 1). All transfer lines after the reactor were heated and the combined stream of FT product and unreacted gases were collected in evacuated, hot glass ampoules and analyzed (Section 2.4) using a method described by Schulz and Nehren [19]. The total liquid product was finally cooled, collected in a cold trap and used for additional analysis (Section 2.4). It should be noted that the ammonia levels in this study were relatively high as it was the intention to study the effect of ammonia systematically, despite the fact that activity may be affected negatively. While these high concentrations may not be necessary to achieve selectivity changes they are also guided by findings from studies on amination of alcohols, a reaction that may be related to reactions steps occurring when ammonia is present during FTS (see also Section 3 and [17]).

### 2.3. Fischer–Tropsch experiments in a fixed bed reactor

The influence of ammonia on olefin selectivity in a fixed-bed reactor was investigated using the 15 wt% Co/ $\text{SiO}_2$  and 15 wt% Fe/ $\text{SiO}_2$  catalysts. For the catalytic runs, 165 mg of catalyst was loaded into a 1/4 in. stainless steel tube reactor and reduced in-situ prior the reaction. For this, the reactor temperature was ramped at  $10^\circ\text{C}/\text{min}$  to  $500^\circ\text{C}$  with 60 mL/min hydrogen and held at the final temperature for 9 h. The reactor was pressurized to 5 bar and heated to reaction temperature ( $170^\circ\text{C}$  for cobalt and  $300^\circ\text{C}$  for iron catalyst). A total synthesis gas flow rate of 10 mL/min was adjusted ( $\text{H}_2:\text{CO}:\text{N}_2 = 2:1:1$ ). In order to study the impact of ammonia on selectivity to olefins, nitrogen was then replaced by the same amount of  $\text{NH}_3$  giving a synthesis gas of ( $\text{H}_2:\text{CO}:\text{NH}_3 = 2:1:1$ ). The transfer lines after the reactor were heated and connected to a 6-port valve, which allowed for online sampling using gas chromatographic techniques (Section 2.4).

Table 1

Different ammonia concentrations and  $\text{H}_2:\text{CO}$  ratios used during the Fischer–Tropsch experiments in the liquid phase.

$\text{NH}_3$ in the synthesis gas feed (vol%)	$\text{H}_2:\text{CO}$ ratio at the reactor inlet
0	2.00
2	1.93
5	1.86
13	1.60
26	1.20

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