



Formation of nitrogen containing compounds from ammonia co-fed to the Fischer–Tropsch synthesis



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ABSTRACT

The effect of ammonia on activity and selectivity of a low temperature, iron-catalyzed slurry phase Fischer–Tropsch process was studied. The ammonia content in the feed was varied systematically from 0 to 10 vol% while the total pressure was adjusted simultaneously in order to keep partial pressures constant. In addition to standard Fischer–Tropsch synthesis (FTS) products, long chained aliphatic amines, nitriles and amides were formed; the latter two product classes had not been observed by others before with iron based catalysts. The selectivities toward nitrogen containing compounds increased with increasing ammonia content while the formation rates of alcohols, aldehydes and organic acids were reduced possibly suggesting that nitrogen containing compounds are formed via oxygenates or their precursors. Common FTS descriptors such as methane selectivity, chain growth probability, olefin to paraffin ratio and double bond shift were largely unaffected at the studied levels of ammonia addition, while the activity at ammonia levels above 2 vol% decreased over and above the intrinsic deactivation rate. Although this deactivation seems reversible upon removal of ammonia from the feed gas, the selectivity is shifted toward higher water gas shift reactivity.

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1. Introduction

The Fischer–Tropsch synthesis, pioneered by Franz Fischer and Hans Tropsch in the early 1900s [1–6], is nowadays a large scale industrial process for the production of straight chained hydrocarbons [7,8]. Although the raw material, synthesis gas, can be sourced from all organic matter, i.e. fossil as well as renewable sources [9–11], the industrial application is focusing on either coal or natural gas as feedstock [7,12]. The currently developing market for cheap methane, sourced from worldwide fracking efforts, has resulted in a revived interest in the process [13]. Industrial applications of the FTS are currently focusing mainly on the production of transportation fuel derived via hydrocracking of waxes to yield high quality diesel and via product isomerization to yield petrol. Only a small fraction of the industrial FT facilities, notably the Sasol plant in Secunda/South Africa, is aimed at the production of high value chemicals including straight chained α -olefins as well as alcohols, aldehydes, ketones and carboxylic acids [12].

A possibility to further increase the profitability of an FT plant via addition of value to FT products is the formation of nitrogen containing compounds, more specifically linear amines, via co-feeding of ammonia (typically 0.5–2 vol%) during the iron-catalyzed synthesis [14–18]. Besides linear amines, solid ammonium carbonate was found in the product stream as well during ammonia feeding by Clark [18]. Predominantly primary amines were also obtained by Kölbl et al. [16,19] in experiments with promoted iron catalysts and ammonia co-feeding (1 vol%) at Kölbl-Engelhardt conditions, where water steam was fed instead of hydrogen. Amines are typically produced via amination of alcohols, notably at reaction conditions similar to those of the FT reaction [20–25]. At significantly harsher conditions with higher temperatures (350–600 °C) and ammonia concentrations of up to 65 vol% selective formation of acetonitrile was observed by several researchers upon co-feeding of ammonia to synthesis gas using transition metal catalysts [26–29].

Organic nitrogen-containing compounds are of great importance in nature as well as to today's societies' daily life. The industrial production of these product classes has hence developed to an essential branch in chemical industry, with production capacities of several million tons per year of amino acids as dietary supplement or pet food [30]. Amines, nitriles or amides are key chemicals and are used as pharmaceuticals, agricultural chemicals,

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solvents or intermediates in a number of industrial applications [22–24]. Many production routes to nitrogen containing compounds are currently available and are mostly heterogeneously catalyzed. As nitrogen sources ammonia, alkyl amines as well as hydrogen cyanide are employed. The hydroamination of alcohols by ammonia or other amines plays an essential role in the industrial production of amines. Nitriles and hydrocarbons are formed in addition as side products [20–25]. This reaction is somewhat related to the Fischer–Tropsch synthesis since similar catalysts are employed and experimentally identified surface reactions as well as hypothesized reaction mechanisms show similarities to the FT synthesis [25,31].

In this study we revisited the addition of ammonia to the iron-catalyzed FT synthesis with emphasis on detailed product analysis. The studies were conducted in a slurry reactor, and contrary to previous studies the amount of ammonia in the feed was increased systematically up to 10 vol% while increasing the total reactor pressure correspondingly. In doing so, this reactor system is ideally suited for studying one reaction parameter only (in this case the ammonia concentration) while all other parameters were kept constant.

2. Experimental

2.1. Catalyst preparation

A precipitated, unsupported iron catalyst was prepared from a hot (90 °C) aqueous 1 M Fe(NO₃)₃·9H₂O (Sigma–Aldrich Inc.) solution. Precipitation was achieved via the addition of a warm (60 °C) aqueous 10 M (NH₄)₂CO₃ (30 % as NH₃, Fluka) solution (pH 7 at the end of the preparation). After repeated washing of the precipitate with boiling de-ionized water, the catalyst was dried overnight at 120 °C. The dried catalyst was then crushed to a particle size of $d_p < 125 \mu\text{m}$ and calcined in a fluidized bed under air (120 ml_{NTP}/min/g_{Fe}) at 350 °C for 4 h (heating rate: 10 °C/min). The catalyst was promoted with potassium via impregnation with an aqueous 1 M solution of KNO₃ (Kimix) targeting a Fe:K ratio of 100:2. The mixture was dried under vacuum in a rotary evaporator. Analysis of the calcined and promoted catalyst showed an Fe:K ratio of 100: 1.5 and a BET area of 30 m²/g_{catalyst}, or 45 m²/g_{Fe}, respectively.

2.2. Catalyst testing

Prior to exposure to FT synthesis conditions, 3.2 g of the prepared catalyst were reduced externally in a fluidized bed reactor at 350 °C for 16 h (heating rate: 1 °C/min) in a hydrogen flow of 67 ml_{NTP}/g_{Fe} min yielding the activated/reduced catalyst containing 2 g of iron, assuming complete reduction. The reduced catalyst was transferred under an inert argon atmosphere into a melt of 5 g of Sasol paraffin wax ('H1', carbon number >30, melting point approx. 112 °C). After cooling, this process resulted in a solid wax tablet protecting the reduced catalyst from contact with air.

The FT synthesis was carried out in a 600 ml stirred slurry reactor (Parr Instruments 452HC03) equipped with a magnetic stirrer drive (Parr instruments A1120HC). Reactor temperature, synthesis gas feed rate and synthesis gas pressure in the feed gas were kept constant at 250 °C, 75 ml_{NTP}/min, H₂:CO = 2 and 5 bar, respectively. The catalyst-wax tablet was added to 270 g of molten Sasol paraffin wax under an argon atmosphere. Gaseous ammonia was fed using a hydrogen–ammonia mixture. Its content in the feed was varied from 0 to 10 vol%, with the total gas flow and the reactor pressure varying proportionally to maintain a synthesis gas partial pressure of 5 bar (see Table 1). Each condition was maintained for 48 h to allow pseudo steady-state to be achieved. Samples

Table 1
Feed gas composition and reactor pressure conditions.

Ammonia content in feed (vol%)	Total feed gas flow rate (ml _{NTP} /min g _{Fe})	P _{reactor} (bar)
0	75.0	5.0
2	76.5	5.1
5	79.0	5.3
10	83.3	5.6

of volatile products (at reaction conditions) were collected using the ampoule method [32] and analyzed at the end of each 48 h period. Liquid samples in the ice cooled cold trap were collected over the last 24 h period of each test condition and also analyzed. The 'base case' condition with no co-feeding of ammonia was revisited after the ammonia addition experiments in order to ascertain potential changes of the catalyst performance. Nitrogen and cyclohexane (0.15% cyclohexane in nitrogen) were injected downstream of the reactor as internal standards for the online GC-TCD and offline GC-FID/MS analyses, respectively. A detailed description of the experimental set-up was given by Claeys et al. [33].

2.3. Analytical methods

The analysis of the feed and the effluent gas for determination of the CO, H₂, CO₂ and CH₄ concentrations was conducted online using a Varian 3600 GC equipped with a thermal conductivity detector. The separation was conducted on a 1.5 m packed, Carbosieve II column (i.d. 2 mm) with argon as the carrier gas operating at isothermal conditions (150 °C).

Ampoule samples of the volatile organic compounds and liquid products from the cold trap were analyzed offline using an HP6890 GC equipped with two identical parallel OV-1-type capillary columns (60 m × 250 μm) connected to a mass spectrometer (MS) and a flame ionization detector (FID), respectively. Selectivities of hydrocarbons, oxygenates and nitrogen containing compounds were calculated based on the formation rates obtained from the C₁–C₂₀ fraction analyzed from the various gas and liquid samples in the GC-FID. The signal obtained with the MS detector was only used for product identification purposes, while the quantification was conducted with the FID signal owing to the highly linear response of this detector type.

3. Results and discussion

In order to validate the effect of ammonia addition to the Fischer–Tropsch synthesis we initially compare classic FTS descriptors such as activity, methane selectivity, chain growth probability, olefin to paraffin ratio, olefin isomerization, i.e. double bond shift, as well as water gas shift (WGS) activity with and without the addition of ammonia. This is then followed by detailing the nature and content of nitrogen containing compounds in the product spectrum as function of ammonia levels in the feed.

3.1. Fischer–Tropsch synthesis

3.1.1. Conversion, WGS and deactivation

After 90 h time on stream (TOS) under Fischer–Tropsch conditions the catalyst displays a steady deactivation behavior from approximately 82% to 75% CO conversion (see Fig. 1). A similar behavior has been previously reported for cobalt and iron FT catalysts [34,35] with poisoning by sulfur [36], reversible poisoning by nitrogen compounds [37], deposition of carbon [35,38], oxidation by product water [35] and sintering [38] described as the contributing drivers for the observed loss in activity. For iron based

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