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## Effects of co-feeding with nitrogen-containing compounds on the performance of supported cobalt and iron catalysts in Fischer–Tropsch synthesis

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### ABSTRACT

The performance of supported cobalt and iron catalysts in low and high temperature Fischer–Tropsch synthesis was investigated in the presence of small amounts of ammonia in syngas. Ammonia was co-fed to the reactor either by in-situ hydrolysis of acetonitrile or by addition of aqueous ammonia.

The addition of acetonitrile and ammonia resulted in significant irreversible deactivation of alumina supported cobalt catalysts. Lower methane and higher C<sub>5+</sub> hydrocarbon selectivities were observed. Iron based catalysts did not show any noticeable deactivation in the presence of acetonitrile or ammonia. Moreover, Fischer–Tropsch reaction rate slightly increased after addition of the nitrogen-containing compounds to silica and alumina supported samples. Lower methane selectivity and higher C<sub>2</sub>–C<sub>4</sub> olefin to paraffin ratio were observed in the presence of ammonia when the catalysts were reduced in hydrogen. Iron catalysts activated in carbon monoxide did not demonstrate any significant effect of ammonia on the selectivity. The catalytic data were explained by irreversible formation of inactive cobalt nitrides in cobalt catalysts and transformation of metallic iron and iron oxides in the presence of acetonitrile and ammonia into iron nitrides and iron carbides active in Fischer–Tropsch synthesis.

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### 1. Introduction

The Fischer–Tropsch (FT) technology converts syngas produced from coal, natural gas, shell gas and biomass into hydrocarbons and oxygenates which can be further upgraded to fine chemicals and fuels. Both cobalt and iron catalysts are used for FT synthesis on the industrial scale. Cobalt catalysts are the catalysts of choice for low temperature FT synthesis, which produces middle distillates and waxes [1,2], while iron catalysts are mostly used in high temperature FT synthesis [3] which manufactures both fuels and petrochemicals. Catalyst deactivation is a major challenge for both cobalt and iron based FT catalysts [4,5]. The mechanism for catalyst deactivation in FT synthesis often includes a combination of different phenomena: poisoning, surface carbon formation, sintering, carbidization (for cobalt catalysts), oxidation, surface reconstruction, attrition... FT catalysts are particularly sensitive

to the presence of impurities in the reaction feed. Thus, purification of the syngas is an important and often very expensive part of the whole technology.

Continuous depletion to fossil resources and strategy for diversification of energy supplies have led to continuously growing interest in the development of new technologies such as BTL (Biomass-to-Liquids) which aim at producing hydrocarbons and oxygenates from renewable resources (e.g. lignocellulosic biomass and organic waste). The biosyngas can be produced from biomass using gasification. The presence of various impurities and poisons specific of biosyngas and gasification process such as tar, particulates, ammonia, hydrochloric acid and sulphur gases [6] can strongly affect the performance of cobalt and iron FT catalysts. The particularities of FT synthesis with biosyngas have been discussed in several reviews [6–9].

Among these impurities, sulphur compounds may cause irreversible deactivation of FT catalysts. A number of reports [10–17] have recently addressed the effect of sulphur impurities on the stability of iron and cobalt FT catalysts. Much less attention has been paid so far to the effects of nitrogen compounds in syngas on the

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performance and stability of FT catalysts. The effect of ammonia [18,19] on the catalytic performance has been shown to be different for cobalt and iron FT catalysts. The reported results however, have been rather contradictory. Borg et al. [15] studied the catalytic performance of alumina and titania supported catalysts in the presence of 4 ppm of  $\text{NH}_3$  in syngas. No effect of ammonia on the catalytic performance was observed. LeVannes et al. [20] found that nitrogen compounds produce reversible effect on the catalytic performance of cobalt catalysts. The catalyst activity was restored by treatment in pure hydrogen. Pendyala et al. [21] studied the effect of addition of ammonia on the performance of platinum promoted cobalt/alumina catalysts. A significant irreversible catalyst deactivation was observed at ammonia levels from 1 to 1200 ppmw. In addition, in the presence of ammonia, the catalyst exhibited lower methane and higher  $\text{C}_{5+}$  hydrocarbon selectivity which were attributed to selective poisoning of the methanation sites. Ma et al. [22] studied the effect of different ammonia containing compounds on the performance of precipitated iron catalysts in a slurry reactor. No deactivation was observed at low ammonia concentrations, while important catalyst deactivation was observed at concentrations of ammonia higher than 400 ppm. In the work of Sango et al. [23] significant amounts of ammonia (up to 10 wt.%) were added to the syngas feed over unsupported iron catalysts. The catalysts did not show any noticeable deactivation at the ammonia concentration below 2% wt. In addition to the usual FT products such as hydrocarbons and oxygenates, the reaction yielded long chained aliphatic amines, nitriles and amides, while the selectivities to alcohols, aldehydes and organic acids were much lower in the presence of ammonia.

The present report addresses the impact of addition of small amounts of acetonitrile and ammonia (1500 and 2500 ppmv) to the syngas feed on the catalytic performance of supported iron and cobalt catalysts. In particular, the effects of cofed acetonitrile and ammonia on CO conversion, methane, light olefins,  $\text{C}_{5+}$  hydrocarbon selectivities, catalyst stability and catalyst structure are discussed in this work. The catalytic performance has been evaluated in a Flowrence high-throughput system [24] (Avantium<sup>®</sup>) equipped with 16 parallel fixed-bed milli-reactors under typical conditions of low and high temperature FT syntheses.

## 2. Experimental

### 2.1. Catalyst preparation

Commercial  $\gamma$ -alumina containing 5% of silica ( $\text{Al}_2\text{O}_3$ , Siralox SASOL) was used as support for preparation of cobalt catalysts. The catalysts were prepared by incipient wetness impregnation with aqueous solutions of cobalt nitrate. The concentrations of the impregnation solutions were calculated to obtain 15 wt.% cobalt in the final catalysts. The alumina supported catalyst containing 25 wt.% Co was prepared using the two-step impregnation. In case of Pt-promoted samples, an additional incipient wetness impregnation of Co/ $\gamma$ - $\text{Al}_2\text{O}_3$  with aqueous solutions of hydrogen hexachloroplatinate ( $\text{H}_2\text{PtCl}_6$ , (Sigma-Aldrich) was carried out. The platinum content was 0.1 wt.% in the final catalysts. After impregnation and drying the cobalt catalysts were calcined in air flow at 400 °C for 6 h with a 1 °C/min temperature ramping.

Iron catalysts were prepared using commercial amorphous silica ( $\text{SiO}_2$ , CARIACT Q-10, Fuji Silysia), alumina (Siralox, Sasol), activated carbon and carbon nanotubes. Activated carbon (AC) was provided by CEKA S.A., washed and then heated with 1 M solution of nitric acid at 50 °C for 2 h. Multi-wall carbon nanotubes (CNT, purity  $\geq 95\%$ , outer diameter 20–30 nm) were purchased from the Chengdu Limited Company of Organic Chemistry (CCOC) in China. They were prepared by chemical vapour deposition. The raw CNTs

were refluxed for 16 h in concentrated  $\text{HNO}_3$  (65 wt.%) at 120 °C in an oil bath. Then, the mixture was filtered and thoroughly washed with distilled water until the neutral pH was reached. The washed carbon nanotubes were then dried overnight at 100 °C.

The iron catalysts were prepared by incipient wetness impregnation of the relevant supports with aqueous solutions of hydrous iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ). The concentrations of the impregnating solutions were calculated to obtain 10 wt.% iron in the final catalysts. After impregnation the catalysts were dried overnight in an oven at 100 °C. Then the catalysts supported by silica and alumina were calcined in a flow of air, while the carbon supported samples were calcined in nitrogen flow at 400 °C for 6 h with a 1 °C/min temperature ramping.

The catalysts are labelled as Mx%/Support, where x indicates metal content in the catalyst, M stands for metal (Co or Fe) and Support specifies the support used ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , AC or CNT). The platinum content is indicated in the Pt-promoted catalysts.

### 2.2. Characterization techniques

The BET surface area, pore volume and average pore diameter were determined by  $\text{N}_2$  physisorption using a Micromeritics ASAP 2000 automated system. The samples were degassed under vacuum at  $<10 \mu\text{m Hg}$  in the Micromeritics ASAP 2000 at 300 °C for 4 h prior to  $\text{N}_2$  physisorption.

The ex situ X-ray powder diffraction (XRD) measurements were conducted using a Bruker AXS D8 diffractometer using  $\text{Cu}(\text{K}\alpha)$  radiation ( $\lambda = 0.1538 \text{ nm}$ ). The XRD patterns were collected in 20–70° ( $2\theta$ ) range. The identification was carried out by comparison with JCPDF standard spectra software. The average crystallite size of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  was calculated using the diffraction lines according to Scherrer's equation [25].

The FTIR spectra were recorded with a Nicolet Protégé 460 FT-IR spectrometer at 4  $\text{cm}^{-1}$  optical resolution. Due to high cobalt content, all catalysts were diluted with  $\alpha$ - $\text{Al}_2\text{O}_3$  (1:1). Prior to the measurements, 20 mg of sample was pressed in self-supporting discs and activated in the IR cell attached to a vacuum line at 400 °C for 4 h followed by reduction in hydrogen at 400 °C. After the reduction, water formed was evacuated at 400 °C for 1 h. Dose per dose adsorption of CO was carried out in the low-temperature cell in liquid nitrogen. In several experiments, the catalysts were pre-treated *in situ* with  $\text{NH}_3$  at 280 °C. Spectra processing was performed by OMNIC 7.3 software.

The cobalt catalysts after catalytic tests in a Flowrence high throughput unit conducted in the presence of acetonitrile were characterized by temperature-programmed desorption (TPD). The samples were weighed (50 mg) and loaded in the middle of a quartz tube. Both ends of the quartz tube were sandwiched with quartz wool. The signals were recorded by a mass spectrometer.

The SSITKA apparatus used in this work is described in Ref. [26]. It contains two independent feed lines. The first line is dedicated to unlabeled compounds and tracer ( $\text{CO}$ ,  $\text{H}_2$ , He and Ne), the second one to the isotopic compounds ( $^{13}\text{CO}$ ). The pressure transducers are used to adjust the same pressure drop for both lines. Isotopic switches were realized using a two-position four ways Valco-valve and monitored with QMG 432 Omnistar in the Faraday mode. In the first experiment, the  $\text{Co}25\text{0.1}\text{Pt}/\text{Al}_2\text{O}_3$  catalyst was reduced hydrogen at 400 °C for 3 h and then exposed to syngas ( $\text{H}_2/\text{CO} = 5$ ) at atmospheric pressure at 220 °C. After conducting 13 h of the reaction in the syngas, the periodic switches were performed from  $^{12}\text{CO}/\text{H}_2/\text{He}/\text{Ne}$  to  $^{13}\text{CO}/\text{H}_2/\text{He}$  with simultaneous measurement of the isotopic transient responses. In the second experiment, the catalyst after reduction in hydrogen was exposed to the flow of gaseous  $\text{NH}_3$  at 220 °C and atmospheric pressure for 2 h. Then the ammonia flow was stopped and the syngas with  $\text{H}_2/\text{CO} = 5$  was directed to the catalyst. After conducting 13 h of the FT reaction in

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