The role of carboxylic acid in cobalt Fischer-Tropsch synthesis catalyst deactivation

D. Kistamurthy [a,b,*], A.M. Saib [a], D.J. Moodley [a], H. Preston [a], I.M. Ciobîcă [c],
W. Janse van Rensburg [a,1], J.W. Niemantsverdriet [b,2], C.J. Weststrate [c,2]

[a] Sasol Technology (Pty) Ltd., P.O. Box 1, Sasolburg, 1947, South Africa
[b] Laboratory for Physical Chemistry of Surfaces, Eindhoven University of Technology, 5600 MB, Eindhoven, The Netherlands
[c] Sasol Technology Netherlands BV, Vlierstraat 111, 7544 GG, Enschede, The Netherlands

ABSTRACT

Oxygenated compounds have previously been detected on spent Co/Al_2O_3 FTS catalyst and have also been proposed to be precursors for carbon formation. Build-up of polymeric carbon on the catalyst during Fischer-Tropsch synthesis (FTS) can negatively influence activity over an extended reaction time. Adsorbed oxygenates detected on spent $Co/\gamma-Al_2O_3$ FTS catalyst are deduced to be located on the $\gamma-Al_2O_3$ support using attenuated total reflectance infrared spectroscopy (ATR-IR). The formation of a metal-carboxylate compound is not detected (ATR-IR) and deduced to be unlikely since acetic acid decomposes at low temperature on a Co metal surface (single crystal $Co(0\,0\,0\,1)$ experiments under ultra-high vacuum conditions). Acetic acid undergoes dissociative adsorption on the $\gamma-Al_2O_3$ $(1\,1\,0)$ and $(1\,0\,0)$ surfaces (DFT), forming an acetate species. Acetic acid vapor, contacted with reduced $Co/Pt/Al_2O_3$ catalyst at model FTS conditions (i.e. 1 bar$_{(a)}$ $H_2/CO:2/1$ at 230 °C), results in predominantly atomic carbon deposition on the catalyst. Co-feeding of excess acetic acid during FTS does not enhance $Co/Pt/Al_2O_3$ catalyst deactivation nor does it significantly impact methane selectivity. Therefore, carboxylic acids can cause atomic carbon formation on $Co/\gamma-Al_2O_3$ catalyst during FTS and result in strongly adsorbed carboxylates on $\gamma-Al_2O_3$ support, but these factors do not significantly impact catalyst deactivation.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The Fischer-Tropsch synthesis (FTS) process involves the transformation of synthesis gas, a mixture of CO and H_2, into long chain hydrocarbon species [1,2]. There is a number of operating FTS plants across the world. For instance, Sasol is involved in large-scale applications of FTS, including two plants in South Africa which have a combined capacity of ~165,000 barrels per day and the ORYX GTL plant in Qatar with a capacity of ~34,000 barrels per day [3]. Shell is also involved in large-scale FTS plants, one located in Qatar with a capacity of ~140,000 barrels per day and another located in Malaysia producing ~14,500 barrels per day [3]. Cobalt-based catalysts are utilized in commercial FTS processes. However, as is

the challenge with many catalysts, the Co FTS catalyst deactivates over time. Stable catalyst performance is vital to the economics of a GTL process, making catalyst deactivation an important research topic in industrial catalyst development.

The factors that contribute to Co FTS catalyst deactivation have been extensively reviewed in the literature [4,5]. Saib et al., for instance, deduced that the deactivation of a $Co/Pt/Al_2O_3$ catalyst is due to a complex interplay of mechanisms which act together but on different time scales [6]. In that study, the dominant deactivation mechanisms under typical Co-catalyzed FTS conditions were postulated to be sintering and carbon formation [6]. On the topic of sintering, we have recently reported that Co nanoparticles undergo Ostwald ripening when exposed to low-conversion FTS conditions [7]. Loss of metal surface area was deduced to proceed *via* diffusion of cobalt-subcarbonyl species over the support surface.

Moodley et al. reviewed the role of carbon formation on Co FTS catalyst deactivation [8,9]. Three different carbon species were identified when temperature-programmed hydrogenation mass spectrometry (TPH-MS) experiments were carried out on spent $Co/Pt/Al_2O_3$ FTS catalyst. The carbon species were assigned to

atomic carbon, residual wax in the pores of the alumina support and polymeric carbon (which refers to hydrogen-lean chains of carbon atoms connected by covalent bonds). Energy-filtered transmission electron microscopy (EFTEM) identified that polymeric carbon was present on both the cobalt and the alumina support. Support-bound carbon was postulated to be the result of carbon spillover from the metal onto the support. H_2 chemisorption experiments showed a correlation between loss of metal surface area and an increase in polymeric carbon with time on line. Thus, it was concluded that polymeric carbon could contribute to longer term deactivation in extended runs of FTS. Further evidence was provided by Weststrate et al. where polymeric carbon, formed *via* an ethylene treatment over a fresh Co/Al_2O_3 catalyst, was shown to be detrimental for catalyst activity [10].

FTS produces not only the desired higher hydrocarbons, but also water and relatively small quantities of side-products which are oxygenated compounds such as carboxylic acids, alcohols, esters and ketones [11,12]. Carboxylic acids comprise a small quantity of the FTS liquid products of which typically acetic acid is the most abundant [13–15]. Pinard et al. analyzed the carbon species on spent $Co-Ru/Al_2O_3$ FTS catalyst [16]. Carbon extracted from the spent catalyst was found to consist of both carboxylic acids (~C4–C24 on a 7 day old catalyst) and alcohols (~C12–C32 on a 7 day old catalyst). TPH-IR indicated that complete removal of carboxylate species required temperatures above 600 °C. Carboxylic acids (C1–C7 acids) adsorbed on pure γ-Al_2O_3 showed infrared (IR) frequencies in the same IR region (corresponding to O-containing molecules) as those of spent $Co/Ru/Al_2O_3$ FTS catalyst. Organic acids were deduced to adsorb strongly on the support or on the metal, which would lead to deactivation if acids blocked active cobalt metal sites.

The objective of the present study is to determine whether carboxylic acids contribute to catalyst deactivation. This is achieved by investigating (i) polymeric carbon formation from carboxylic acid over a Co/Al_2O_3 FTS catalyst, (ii) the effect of acid co-feeding during Co-catalyzed FTS and (iii) the location (Co metal and/or γ-Al_2O_3 support) of the carboxylate species identified on spent catalyst.

2. Materials and methods

Acetic acid (99%) was purchased from Sigma–Aldrich and used as received. γ-Al_2O_3 support material was supplied by Sasol Germany. Fresh $Co/Pt/\gamma$-Al_2O_3 catalyst (20 wt% Co, 0.05 wt% platinum) was obtained from Sasol. The catalyst was prepared by slurry impregnation of the γ-Al_2O_3 support with an aqueous cobalt nitrate and ammonium platinum nitrate solution. After impregnation and drying, the catalyst precursor was calcined (at 250 °C in air) and this procedure was repeated to achieve the desired metal loading [17–20]. The catalyst was reduced (in pure H_2 at 425 °C) and embedded in wax (Sasol H1 wax, density 0.94 g/cm^3) before FTS testing.

Spent $Co/Pt/Al_2O_3$ FTS catalyst samples were supplied by Sasol. The samples were removed from a pilot plant scale slurry bubble column FTS reactor in Sasolburg, South Africa, operated at relevant FTS conditions. Sample was removed (after 90 days on line) and contained a protective wax layer. Before further analysis, a wax extraction procedure was carried out according to the procedure described by Moodley et al. [9].

Acetic acid was adsorbed on γ-Al_2O_3 by adding (10 ml) of an aqueous acetic acid solution (5 vol%, room temperature) to γ-Al_2O_3 (2 g) which was pre-dried at 120 °C for 10 min. The resulting suspension was stirred (1 min) before the excess solution was filtered off and the sample dried (for 10 min) at 120 °C in air.

Acetic acid saturated synthesis gas was obtained by flowing H_2 (10 ml(NTP)/min), CO (5 ml(NTP)/min) and Ar (90 ml(NTP)/min) gas

through a stainless steel saturator filled with pure (99%) acetic acid (25 ml) which was kept at room temperature (~0.02 bar vapor pressure of acetic acid at RT as determined in Ref. [21]). The acetic acid saturated gas was led over the sample of either γ-Al_2O_3 or $Co/Pt/Al_2O_3$ catalyst (100 mg). The sample was loaded and enclosed with glass wool in a quartz glass reactor tube (4 mm internal diameter). The reactor tube was contained in an oven that was used to heat the sample evenly. The reactor tube contained two separate inlet connections, one for acid saturated gas and the other for acid-free gas. All treatments were carried out at atmospheric pressure. The Co-catalyst sample was pre-reduced at 425 °C (5 °C/min, 4 h) under 10% H_2/Ar, followed by cooling to 230 °C in the same gas mixture. Once 230 °C was reached, the feed gas was changed to acid-saturated H_2/Ar gas and CO was introduced to the gas mixture (for a H_2/CO ratio of 2) at this point as well. The samples were exposed to this gas mixture for 15 min, after which time the feed gas was changed back to acid-free H_2/Ar gas, which was flowed for 1 h at 230 °C to ensure acid was removed from the reactor tube (as monitored by MS). The sample was then cooled to room temperature under H_2/Ar gas flow.

In the cases where in situ temperature programmed (TP) experiments coupled with mass spectrometry (MS) was carried out, samples were cooled in H_2/Ar and kept under H_2/Ar gas flow at room temperature until the TPH-MS measurement was carried out. Those measurements were carried out by heating the sample to 800 °C (5 °C/min) using 10% H_2/Ar (50 ml(NTP)/min). The evolving gases were monitored using a Omnistar^{TM} Thermostar^{TM} GSD 320 mass spectrometer.

In the cases where ex situ TPH-MS and ATR-IR was carried out, samples were slowly exposed to air after cooling to room temperature. This was done by stopping the gas flow and opening the narrow inlet and outlet openings of the reactor which enabled air to slowly replace the H_2/Ar mixture in the reactor tube. Samples were then unloaded in air and used for measurements.

For ex situ TP-MS measurements, samples were packed into a quartz glass reactor tube (4 mm ID) and enclosed with glass wool. Measurements were carried out by heating samples to 800 °C (5 °C/min) using 10% H_2/He (50 ml(NTP)/min total flow) in the case of TPH-MS and pure He (50 ml(NTP)/min) in the case of TPD-MS. The evolving gases were monitored using a Balzers QMA 400 mass spectrometer.

TPD-MS coupled with GC-MS was carried out on sample of acetic acid adsorbed on γ-Al_2O_3. The sample (700 mg) was packed in a fixed bed reactor (catalyst bed 800 by 5 mm) and enclosed with SiC (using a quantity that filled the rest of the catalyst bed volume). The reactor was heated under Ar (50 ml(NTP)/min) to 500 °C (2 °C/min). GC-MS was carried out using a Varian CP-Pora-BondQ column (L = 50 m, ID 0.32 mm) with He as a carrier gas and a sampling temperature program of 240 °C (5 °C/min) for 10 min.

Attenuated total reflectance infrared spectroscopy (ATR-IR) spectra were recorded using a Nicolet Smart Golden gate instrument equipped with a diamond crystal (cutoff at 800 cm^{-1}). Measurements were carried out in transmission mode with a resolution of 2 cm^{-1} over 128 scans.

Decomposition of acetic acid on the Co(0 0 0 1) surface was studied in a UHV system described in detail elsewhere [22]. In brief, the Co sample is clamped between two W wires, which were used for resistive heating and cooling down to 80–90 K using liquid nitrogen. The sample was cleaned by sputtering at 630 K (20–30 min, 1 kV Ar$^+$) followed by 20–30 min of annealing in vacuum at 630 K. Sample cleanliness was routinely checked using hydrogen TPD, which is sensitive to the presence of defects and contaminants such as C and O, as well as CO TPD, which is sensitive to C, O and S contaminations [23,24]. A typical heating rate of 0.5 K/s was used to match the relatively low sampling frequency of the Kelvin probe. Relative work function values are reported with respect to the clean