Applied Catalysis A: General 354 (2009) 102–110

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Carbon deposition as a deactivation mechanism of cobalt-based Fischer–Tropsch synthesis catalysts under realistic conditions

D.J. Moodley [a,b,*], J. van de Loosdrecht [b], A.M. Saib [b], M.J. Overett [b],
A.K. Datye [c], J.W. Niemantsverdriet [a]

[a] *Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, Eindhoven 5600 MB, Brabant, The Netherlands*
[b] *Sasol Technology, P.O. Box 1, Sasolburg 1947, South Africa*
[c] *Department of Chemical and Nuclear Engineering and Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM 87131, USA*

ARTICLE INFO

Article history:
Received 23 June 2008
Received in revised form 17 November 2008
Accepted 17 November 2008
Available online 25 November 2008

Keywords:
Cobalt
Fischer–Tropsch
Carbon
Deactivation
EFTEM
Gas-to-liquid

ABSTRACT

Deactivation of cobalt-based Fischer–Tropsch synthesis (FTS) catalysts by carbonaceous species has been previously postulated. This mechanism, however, is difficult to prove due to the presence of long chain hydrocarbon wax product and the potential accumulation of inactive carbon on the catalyst support. Furthermore, due to the slow build-up of low quantities of inactive carbon with time on stream, the investigation of carbon deposition necessitates the use of data from extended FTS runs. In this study, the formation of carbon deposits on samples of a $Co/Pt/Al_2O_3$ catalyst, taken from a 100-barrel/day slurry bubble column reactor operated over a period of 6 months at commercially relevant FTS conditions is reported. The spent catalysts were wax extracted in an inert environment and the amount, nature and location of carbon deposits were then studied using temperature programmed hydrogenation and oxidation (TPH/TPO), energy filtered transmission electron microscopy (EFTEM), high sensitivity low energy ion scattering (HS-LEIS) and hydrogen chemisorption. TPH/TPO showed that there is an increase in polymeric carbon with time on stream which may account for a part of the observed long-term catalyst deactivation. Carbon maps from EFTEM as well HS-LEIS data show that the polymeric carbon is located both on the alumina support and cobalt. Although there is clearly an interplay of various deactivation mechanisms which may also include sintering, poisoning and cobalt reconstruction, the evidence presented shows that the polymeric carbon on the metal may be linked with a part of the longer term catalyst deactivation.

1. Introduction

The Fischer–Tropsch synthesis (FTS) is at the heart of the gas-to-liquid (GTL) process, which involves the conversion of synthesis gas derived from natural gas to clean environmentally friendly diesel [1], i.e. low in sulphur and aromatics. Cobalt-based catalysts supported on oxidic carriers are preferred to iron for this industrial process due to their high per pass FT activity, low oxygenate and CO_2 selectivity [2]. However, cobalt-based FT catalysts are more expensive compared to iron-based catalysts and therefore a long catalyst lifetime is needed to ensure that the process is economically feasible [3]. On a commercial scale, Shell is operating a supported cobalt catalyst in a fixed bed reactor, as part of their shell middle distillate synthesis (SMDS) process in Bintulu, Malaysia. Sasol has a 34,000-barrel/day GTL plant in operation in Ras Laffan, Qatar, which is based on the Sasol Slurry Phase Distillate^{TM} (Sasol SPD^{TM}) process, using a supported cobalt catalyst in a slurry bed.

Cobalt-based catalysts tested under realistic conditions (Fig. 1) exhibit deactivation with time on stream [4,5]. In order to maximize the lifetime of a cobalt catalyst for such processes, an understanding of the deactivation mechanisms at play is paramount. A lot of attention has focused on investigating the role of oxidation of metallic cobalt on catalyst deactivation [4,6–10]. However, recent work on an industrial Co/Al_2O_3 catalyst using XANES, XRD and magnetic measurements has shown that oxidation is not a deactivation mechanism during realistic FTS [4,11]. Other postulated deactivation mechanisms include cobalt support compound formation, poisoning, sintering, cobalt reconstruction and the formation of inert carbonaceous phases [12]. Furthermore, it is likely that the observed deactivation in cobalt-based FTS catalysts results from the interplay of several of the above-mentioned deactivation mechanisms [4].

---

* Corresponding author. Tel.: +31 40 247 5373; fax: +31 40 247 3481.
E-mail address: d.j.moodley@tue.nl (D.J. Moodley).

0926-860X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2008.11.015

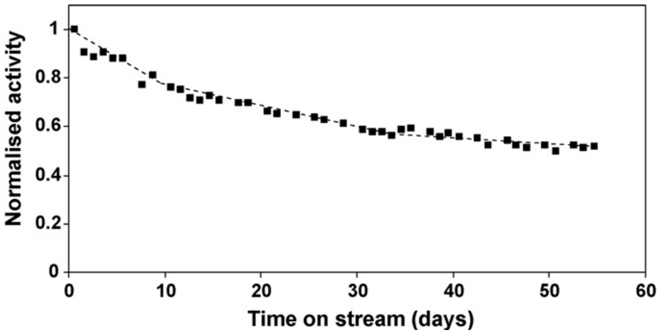

Fig. 1. Normalized activity for a Co/Pt/Al_2O_3 catalyst during realistic Fischer–Tropsch synthesis, i.e. 230 °C, 20 bar, H_2 + CO conversion between 50 and 70%, feed gas composition of 50–60 vol.% H_2 and 30–40 vol.% CO, $P_{H_2O}/P_{H_2} = 1 - 1.5, P_{H_2O} = 4 - 6$ bar (adapted from [4]).

This study focuses on the role of carbon deposition. Menon [13] has classified the Fischer–Tropsch synthesis as a carbon insensitive reaction as there is apparently sufficient hydrogen on the catalyst surface and the strong hydrogenation activity of the catalyst keeps the surface relatively clean and active even when appreciable quantities of carbon are already present on the surface. It is also known that cobalt has a lesser tendency to produce carbon than iron [14]. Even so, a close inspection of the open and patent literature published especially by companies investing in GTL technologies suggests that cobalt-based FTS catalysts are negatively influenced by carbon [15–19]. Syntroleum has reported the slow build-up of polymeric or graphitic carbon with increasing time on stream [15]. Small amounts of the carbon (1 wt%) as determined by TGA-MS, were sufficient to cause blocking of the cobalt active phase after 40 days online. BP also ascribed deactivation on a Co/ZnO catalyst to small amounts of a refractory carbon phase that was present on cobalt [16]. Various regeneration patents also suggested that carbonaceous phases that form during FTS will deactivate the catalyst and need to be removed [17–19]. Also, deactivation of the cobalt active phase by carbonaceous species during laboratory scale CO hydrogenation has been postulated in a few studies [20–22]. This mechanism, however, is difficult to prove in FT synthesis due to the presence of heavy hydrocarbon wax product and the potential spillover and build-up of inert carbon on the catalyst support. Also it is possible that deleterious carbon deposition is kinetically slow during realistic FTS conditions and its effect on activity is only seen during extended runs. Studies have also been conducted on supported cobalt catalysts that suggest deactivation by pore plugging by the heavy wax product [23,24].

There are a number of ways that carbon may interact with a supported cobalt catalyst to affect its activity. The carbon deposits may block the catalyst pores resulting in diffusion limitations, poison the metal surface by binding irreversibly or even encapsulate metal particles [25]. Subsurface carbon may also play a role in electronic inhibition of activity [26]. It has also been shown that carbon bound to a metal surface can induce a surface reconstruction which will affect the activity [27]. The diffusion of carbon into cobalt can also result in the formation of bulk cobalt carbide [28]. Bulk cobalt carbide is not considered FT active and results in both activity and selectivity loss, presumably through electronic inhibition that affects the dissociation of CO [29,30]. It has been shown that bulk carbide can form during conditions where hydrogen is depleted [31]. It has been reported that bulk carbides are thermodynamically unstable during the synthesis (200–240 °C) however, they have been previously observed on cobalt FTS catalysts using in situ [32] and synchrotron XRD [33].

In this study we report on the formation of carbon deposits as a deactivation mechanism on Co/Pt/Al_2O_3 catalyst samples taken from a demonstration run performed at realistic FTS conditions. The spent catalysts were wax extracted in an inert environment and were then characterized. The accumulation, location and nature of the carbon deposits was investigated using X-ray photoelectron spectroscopy analysis (XPS), temperature programmed (TPO/TPH) techniques, hydrogen chemisorption, energy filtered transmission electron microscopy (EFTEM) and high sensitivity low energy ion scattering (HS-LEIS).

2. Experimental

2.1. Catalyst preparation

A 20 wt% Co/Al_2O_3 catalyst, promoted with 0.05 wt% platinum, was prepared by slurry impregnation of a γ-alumina support (Puralox 5/150 from Sasol, Germany) with an aqueous cobalt nitrate solution, also containing the platinum precursor (ammonium platinum nitrate). After impregnation and drying, the catalyst intermediate was calcined at 250 °C in air and reduced in pure hydrogen at 425 °C. To achieve the required cobalt loading two impregnation and calcination steps were performed [34–38].

2.2. Extended catalyst testing in demonstration unit run

The Co/Pt/Al_2O_3 catalyst was tested in a 100 barrel/day slurry bubble column reactor with a diameter of 0.9 m at commercially relevant FTS conditions, i.e. 230 °C, 20 bar, H_2 + CO conversion between 50 and 70%, feed gas composition of 50–60 vol.% H_2 and 30–40 vol.% CO. The reactor was well-mixed ensuring that representative samples were taken each time.

2.3. Wax extraction procedure

Samples of spent catalyst, protected in a wax layer, were taken from the reactor at various time intervals under an inert nitrogen environment and allowed to congeal. Ideally, the cobalt catalysts should be analyzed for carbon deposits in a pseudo-in situ manner; however, this is not possible as due to the presence of a large amount of hydrocarbon wax present. This wax, if present in large amounts will interfere with the follow-up analysis for carbon; for example it may attenuate electrons in XPS and transmission electron microscopy (TEM), or be transformed to other forms of carbon in Temperature programmed hydrogenation (TPH) due to the exothermic burn off. The wax layer was thus removed down to low levels in a controlled manner by an exhaustive extraction, at mild conditions with dry, deoxygenated tetrahydrofuran (THF, b.p. 66 °C) under an inert, argon (99.999%) environment for around 3 h, using a P40 glass frit. After extraction the obtained catalyst particles were dried under vacuum at room temperature to remove the THF. The catalyst was then transferred under vacuum using Schlenk glassware into a glovebox (4 ppm O_2, 1 ppm H_2O). The total carbon level after extraction was on average about 4 wt% as determined by LECO elemental analysis. An important aspect of the wax-extraction procedure was that it should not alter the reactivity of carbon species present on the catalysts. A comparison between a TPH (as outlined in Section 2.5) of a wax-covered catalyst, as sampled from the reactor and a catalyst wax-extracted in the inert environment at the mild conditions described above, showed that the extraction resulted in the removal of a large part of the wax, and not a change in the reactivity of the carbon.

2.4. X-ray photoelectron spectroscopy analysis (XPS)

The samples were prepared in the glovebox by crushing the wax-extracted, FTS catalyst samples in a pestle and mortar. Afterwards, the powders were pressed into an indium layer on top