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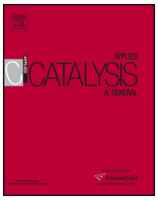

X-ray absorption, X-ray diffraction and electron microscopy study of spent cobalt based catalyst in semi-commercial scale Fischer–Tropsch synthesis

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ABSTRACT

Calcined, reduced and spent Co-Re/γ-Al_2O_3 catalysts for Fischer–Tropsch synthesis (FTS) were characterized and compared. Co-K-edge and Re-L_{III}-edge X-ray absorption near edge structure (XANES), X-ray powder diffraction (XRPD), transmission electron microscopy (TEM) and H_2 chemisorption were used to provide insight into structural transformations that the catalyst experiences during a month of operation in a semi-commercial FTS plant. Results from the core techniques for nanoparticle size determination suggest that sintering of the cobalt crystallites is an important deactivation mechanism in FTS performed in slurry reactors. In addition, a higher degree of reduction is observed for the spent catalytic material, while Re appears in a partially reduced state before and after reaction. The particle size distribution together with the spread of Co nanoparticles on the γ-Al_2O_3 surface indicates crystallite migration as the prevailing mechanism.

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1. Introduction

The gas-to-liquid (GTL) process is the conversion of natural gas derived synthesis gas into hydrocarbons via Fischer–Tropsch synthesis (FTS) [1]. In recent years large investments have been made in the field of GTL with the Oryx and Pearl plants in Qatar to be the latest achievements. This dynamic growth is further supported by new technologies for exploiting unconventional gas sources that have allowed larger amounts of natural gas to reach the market. A higher gas supply might increase the price difference of crude oil and natural gas, which will likely trigger more research and applications in the area of GTL [2].

The currently commercialized GTL technologies use supported cobalt catalysts for the Fischer–Tropsch synthesis step, in which CO and H_2 are transformed to a wide range of linear long-chain hydrocarbons and water [3]. One of the challenges in applied Co-based FTS is the lifetime of the catalyst. Due to the relatively high price of cobalt, continuous operation without catalyst replacement for long periods is favourable and, therefore, a lot of effort has been made towards understanding catalyst deactivation [4] and regeneration phenomena [5]. The deactivation profile of Co-FTS is characterized by two regimes of different deactivation rate and degree of reversibility [6]. The partial reversibility of the activity loss during different time on stream upon mild H_2 treatments suggests that more than one deactivation mechanism contributes to the deactivation profile. Deactivation with irreversible character is of high industrial significance. Moreover, due to the narrow operational window of FTS and the correlation of conversion level and deactivation rate, which may lead to several deactivation pathways, investigation through accelerated deactivation tests is difficult. As a result of the slow development of such phenomena extended FTS runs lasting several weeks to months are required and hence the detailed study of FTS deactivation in the long term dictates collaboration between industry and academia.

Although GTL today can be regarded as proven technology there is a lack of information on long term deactivation and one should go back in time to find information on the industrial scale [7]. The number of publications and reports dealing with characterization

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of catalysts used in extended FTS trials (>500 h) is limited. Published information suggests that sintering of cobalt particles [8–10], formation of inactive cobalt-support mixed phases [10,11] and formation of stable carbon species [12–15] can be the main cause of the “irreversible” catalyst deactivation in FTS.

In the present study a spent catalyst operated in a semi-commercial demonstration GTL unit with production capacity of 1000 bpd [16] was analysed and compared to its fresh analogue. The Co-Re/γ-Al_2O_3 catalyst sample was unloaded from the slurry reactor after a month of operation at commercial FTS conditions. Ex situ and quasi in situ characterization techniques were employed in order to reveal changes that occurred during operation and assist towards the understanding of the deactivation mechanism at the industrial scale.

2. Experimental

2.1. Catalyst preparation

The nominal composition of prepared catalysts for laboratory use was 20 wt.% Co and 0.5 wt.% Re supported on γ-Al_2O_3. These catalysts were prepared by one-step aqueous incipient wetness co-impregnation of $Co(NO_3)_2{\cdot}6H_2O$ and $HReO_4$. The support was a Puralox SCCa type material from Sasol GmbH. The laboratory catalysts are dried in air at 393 K for 3 hours and calcined in air at 573 K for 16 h before use. The commercial catalyst investigated in this study was prepared similarly by adapting the laboratory procedure to the use of large scale production equipment. The present study deals with the characterization of the industrial catalyst in different steps of activation and operation; the freshly calcined catalyst (Cat), a reduced catalyst embedded in FT-wax (Cat-R-W) and a spent catalyst (Cat-R-W-FT). The materials were characterized as received and at different stages of the applied post-treatments, i.e. de-waxing and temperature programmed hydrogenation (TPH). All catalysts were provided by Statoil Petroleum AS.

2.2. Hydrogen chemisorption

Hydrogen adsorption isotherms were recorded on a Micromeritics ASAP 2020 unit at 313 K. The samples (0.2 g) were initially treated with He at 393 K for 2 h. Consequently, it was evacuated at 313 K for 1 h, and then reduced in flowing hydrogen at 623 K for 10 h. The temperature was increased at 3 K/min from 313 to 623 K. After reduction, the sample was evacuated for 1 h at 603 K and for 30 min at 373 K before subsequent cooling to 313 K. The adsorption isotherm was recorded at this temperature and was extrapolated to zero pressure where the amount of chemisorbed hydrogen was determined. Furthermore, in order to calculate the dispersion, it was assumed that two cobalt sites are covered by one hydrogen molecule [17] and that rhenium does not contribute to the amount of hydrogen adsorbed. The average diameter of metallic cobalt nanoparticles ($d(Co^0)$, nm) was calculated from the cobalt metal dispersion (D, %) by assuming uniform spherical metal particles (site density of 14.6 at/nm^2).

2.3. Transmission electron microscopy

TEM experiments were performed with a JEOL 2010F equipped with a field emission gun, operating at 200 kV accelerating voltage. TEM samples were prepared by dispersion of the crushed catalysts powder on a carbon supported Cu mesh grid. In order to identify different phases in the samples, both diffraction and high resolution TEM (HRTEM) were applied. Particle size measurements were performed by direct measurements on the TEM images using Digital Micrograph tools.

2.4. X-ray absorption near edge structure

The BM01B station of the Swiss-Norwegian beam lines (SNBL) at the European Synchrotron Radiation Facility (ESRF) was used for the X-ray absorption experiments [18]. XANES spectra were recorded at the Co K-edge (E = 7709 eV) and Re L_{III}-edge (E = 10535.3 eV) using a double crystal Si (1 1 1) monochromator. The data collection was carried out in transmission mode. Ion chamber detectors filled with mixtures of inert gases at ambient temperature and pressure were used for measuring the intensities of the incident (I_0) and transmitted (I_t) X-rays. The energy calibration was done by measuring the spectrum of Co and Re foils. The definition of edge energy was done by taking the observed maximum of the first derivative. Linear combination analysis (LCA) of the XANES spectra obtained from reference materials including Co foil, Co_3O_4, CoO and $CoAl_2O_4$ provide quantified information on the concentration of different phases. Linear combination analysis (LCA) was performed by Athena software, part of the Horae software package (Version 1.2.9) [19].

For the XANES experiments the in situ cell that was used was developed based on previously proposed configurations [20,21]. The detailed design of the cell and description of the experimental set-up can be found elsewhere [22]. In brief a quartz capillary is used as a plug flow reaction cell. The capillary has overall length, outer diameter, and wall thickness of 60 mm, 1 mm, and 0.02 mm, respectively. It is inserted into a stainless steel bracket and glued on its frame. Swagelok fittings are used to connect the bracket with the basic construction of the cell. The catalyst bed is immobilized by quartz wool plugs and lying above a vertical hot air blower. The reactor inlet and outlet are heated up to 423 K by heating cartridges. The chosen cell configuration can accommodate the combination of several X-ray based characterization techniques at industrially relevant conditions [23].

2.5. X-ray powder diffraction

The catalyst was characterized by X-ray powder diffraction (XRPD). The measurements were performed at the BM01A station of the SNBL. In the BM01A station a square X-ray beam of 500 μm was adjusted to a corresponding wavelength of 0.6978 Å. Powder diffraction patterns were collected using a mar345 area detector with a diameter of 345 mm at a sample-to-detector distance of 230 mm. The sample was inserted into a quartz capillary prior analysis. Quartz capillaries of 0.7 mm diameter were used to minimize instrumental broadening [24]. The exposure time was 45 s and the obtained images were converted to normal one-dimensional powder patterns using the program FIT2D [25]. Pawley fit of the obtained data sets was applied with fityk [26] and Topas v 4.2 software [27].

The in situ cell used for the XRPD experiments was based on the design described by Norby [28]. The principle of the cell construction is similar to the one used for the XANES experimentation. In addition one end of the basic construction of the cell can be attached to a goniometer allowing semi-rotating/swinging mode for improved statistics of the recorded pattern. The description of the experimental set-up can be found elsewhere [29].

2.6. Wax extraction (de-waxing)

Wax extraction has been done using a Soxhlet extractor and by using tetrahydrofuran (THF) solvent. Initially the solvent was degassed overnight under the flow of Ar (99.999%) in order to remove dissolved O_2. Subsequently the system was heated to 358 K and left overnight to complete several reflux cycles under Ar atmosphere. Finally the part of the Sohxlet apparatus containing the catalyst was isolated and transferred to a glove-box where the

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