Further insights into the effect of sulfur on the activity and selectivity of cobalt-based Fischer–Tropsch catalysts

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ABSTRACT

A sulfur poisoning study was performed by *ex situ* poisoning of a platinum-promoted cobalt/alumina catalyst with different sulfur amounts. The poisoned catalyst samples were tested at relevant Fischer–Tropsch reaction conditions and at the same CO conversion in order to evaluate the effect of sulfur on catalyst activity and product selectivity. It was found that the activity and the selectivity to long-chain hydrocarbons decrease with increasing sulfur content. Moreover, it was found that sulfur has no significant effect on the CO_2 selectivity. It was also shown that sulfur significantly enhances olefin hydrogenation. Finally, a deactivation model relating the catalyst activity and the sulfur to cobalt active site ratio was proposed and used to describe the experimental results.

1. Introduction

The catalytic conversion of synthesis gas into hydrocarbons (Fischer–Tropsch synthesis, FTS) is receiving great attention due to its potential for converting different carbon sources (coal, natural gas and/or biomass) into liquid transportation fuels [1–3]. It is generally known that sulfur compounds contained in these raw materials are severe poisons for cobalt-based FT catalysts [4–6]. The effect of S on the performance of these catalysts has been investigated and reported in various literature studies [5–10]. Nevertheless, contradictions still exist regarding the effect of this poison on product selectivity.

Sulfur poisoning of FT catalysts has been studied by both *in situ* [5,7,8] and *ex situ* methods [6,9,11–13]. *In situ* methods are challenging [14]. Sulfur carriers, such as H_2S, adsorb strongly on metallic tubes making it very difficult to precisely determine the S amounts reaching the catalyst samples. Moreover, the high adsorption capacity of H_2S may lead to both intraparticle and reactor sulfur concentration gradients [15] which complicates the evaluation and understanding of activity and selectivity data. *Ex situ* procedures consist in sulfiding the catalyst samples with known amounts of S prior to catalyst testing. These methods lead to a more homogeneous sulfur distribution in the catalyst and the

reactor. Nevertheless, *ex situ* procedures may present a different Co–S interaction than that occurring under reaction conditions [6,14].

Among different studies it is noteworthy to present a very respectable work from Visconti et al. [6,16] in which they studied sulfur poisoning by means of an *ex situ* procedure. In this study [6], a γ-Al_2O_3 supported cobalt-based catalyst was impregnated with ammonium sulfide solutions leading to catalyst samples containing sulfur amounts in the range of 0–2000 ppmw. The different poisoned samples were tested under low temperature FT conditions at 20 bar and 503 K for 200–300 h on stream in order to reach steady-state conditions. The effect of S loading on catalyst activity and selectivity was evaluated and a deactivation model was proposed. In order to better simulate the Co–S interaction, the S impregnation was performed on previously reduced samples (where Co is in a reduced state). For that purpose, the catalyst samples were reduced in H_2 in a tubular reactor and subsequently impregnated with an ammonium sulfide solution in an inert atmosphere. The results from their study showed that both the activity and selectivity to long chain hydrocarbons decrease dramatically with increasing sulfur content. Furthermore, the results also showed that sulfur increases the selectivity to olefins and CO_2. Unfortunately, these poisoned samples were tested using the same gas-hourly space velocity (GHSV). As a consequence, different CO conversions and thus different water partial pressures were employed, fact that affects both product selectivity [17] and catalyst stability [18–20].

More recently, Borg et al. [7] studied the effect of *in situ* H_2S addition on a γ-Al_2O_3 supported cobalt-based catalyst at similar FT conditions (20 bar and 483 K). In this work they studied the variation in CO conversion and selectivity with time on stream until nearly complete deactivation of the catalyst (due to complete blockage of Co sites by sulfur atoms together with other intrinsic catalyst deactivation phenomena). The results of this work showed a decrease in selectivity to long-chain hydrocarbons with continuous H_2S addition. Nevertheless, the observed variation in selectivity with CO conversion was in line with that observed in the absence of H_2S. Consequently, they concluded that S has no significant effect on the primary FT product distribution. In contrast with the study from Visconti et al. [6], they concluded that S has no effect on the CO_2 selectivity and that it only a shows a slight enhancement of olefin hydrogenation. Nevertheless, this study was performed in a fixed-bed reactor, fact that results in large S concentration differences in the axial direction. Indeed, it is possible that H_2S was adsorbing on the first part of the reactor leading to, mainly, two different zones in the catalyst bed: one that was completely deactivated and which increases in size with time on stream, and another that behaved as a nearly S-free catalyst. Thus, it could be expected that one would obtain selectivity results similar to those corresponding to an unpoisoned catalyst.

Other literature studies have shown contradictory results. For instance, Bartholomew and Bowman [5] investigated the effect of *in situ* H_2S addition on silica-supported cobalt-based catalysts and observed that the addition of S increased the selectivity toward long-chain hydrocarbons. This phenomenon was explained by a selective adsorption of S on sites which normally adsorb H_2 leading to a slightly H_2 deficient surface. Bambal et al. [21] have recently investigated the effect of organosulfur compounds on silica-supported cobalt-based catalysts. Contrariwise they found that S increases the selectivity to short chain hydrocarbons and olefins. Finally, Pansare and Allison [8] studied the effect of *in situ* $(CH_3)_2S$ addition on an alumina-supported cobalt-based catalyst using a continuously stirred tank reactor. In that work, they claimed that S decreases the selectivity to both long chain hydrocarbons and olefins. Unfortunately, in contrast with the work from Borg et al. [7], these investigations did not provide a more comprehensive discussion considering the effect of CO conversion on selectivity.

In the present study, sulfur was *ex situ* added to a γ-Al_2O_3 supported cobalt-based catalyst. The resulting poisoned samples were tested under relevant low temperature FT conditions at the same CO conversion. The main objective of this work is to clarify this controversial effect of S on product selectivity. This work also provides a catalyst deactivation model in order to predict the catalyst activity in terms of sulfur coverage and atomic sulfur to cobalt ratios.

2. Methods

2.1. Catalyst preparation

A catalyst composed of 12 wt% cobalt and 0.5 wt% platinum supported on γ-Al_2O_3 was prepared by incipient wetness impregnation. Prior to impregnation, the γ-Al_2O_3 (Puralox SCCa-5/200 from Sasol) was calcined in air for 10 h at 773 K (ramp: 1 K/min). After calcination, the support was impregnated with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (ACS reagent, $\geq$98% Sigma Aldrich). Due to the large volume of water required to dissolve the salt, the aqueous solution was deposited batch wise, drying the catalyst samples at 373 K for 2 h after each deposition. A total of 3 batches were needed for complete deposition of the cobalt nitrate aqueous solution. Then, the catalyst was dried and impregnated with an aqueous solution of $Pt(NO_3)_2 \cdot 4NH_3$ (Premion, 99.99% Alfa Aesar). Once more, the deposition was carried out batch wise. A total of

2 batches were needed in order to complete the deposition of the platinum-based aqueous solution. After impregnation the catalyst was dried at 393 K for 3 h and calcined at 573 K for 16 h (ramp: 1 K/min).

S poisoning of the catalyst was carried out by incipient wetness impregnation of an aqueous solution of ammonium sulfide. The method employed for preparing different poisoned samples is that described in the previous work of Visconti et al. [6]. Prior to impregnation, the catalyst was reduced in H_2 flow in a quartz tubular reactor at 623 K for 16 h (ramp: 1 K/min) at atmospheric pressure. After reduction the catalyst was impregnated with different ammonium sulfide solutions in an inert atmosphere. Then, the catalyst was dried at 353 K overnight and finally exposed to air. By using this procedure catalyst samples loaded with 10, 100, 250 and 1000 ppmw of S were prepared. These amounts can be related to different times on stream depending on employed GHSV and the sulfur concentration in synthesis gas. These amounts correspond, respectively, to 250, 2500, 6250 and 25,000 h on stream for a GHSV of 2000 cm^3 (STP)/h/g and a sulfur concentration in synthesis gas of 20 ppbw, assuming that all the sulfur fed in the reactor adsorbs on the catalyst. The samples were named according to their sulfur content, i.e. the sample containing 1000 ppmw of S was named S1000. The fresh catalyst sample (S-free) was named S0.

2.2. Catalyst characterization techniques

Brunauer–Emmet–Teller (BET) surface area and porosity measurements were performed in a Micromeritics ASAP 2000 unit. The samples were degassed and dried at 523 K for one day prior to analysis. The BET surface area was estimated by N_2 adsorption at liquid N_2 temperature at relative pressures between 0.02 and 0.6. The total pore volume was estimated from a single point of adsorption at a relative pressure of 0.998.

Hydrogen temperature-programmed-reduction (TPR) was used to study the catalyst reducibility. The TPR measurements of the calcined catalyst sample were performed in a Micromeritics Autochem 2910. The catalyst samples were heated up to 1203 K (ramp: 10 K/min) in a flow consisting of 5% H_2 in Ar while monitoring the difference in thermal conductivity between the inlet and outlet gas. The thermal conductivity detector (TCD) signal was calibrated by complete reduction of a reference Ag_2O powder in order to calculate the H_2 consumption. The degree of reduction (DOR, %) was estimated by H_2-TPR after *in situ* reduction of the calcined catalyst at 623 K (heating rate: 1 K/min) for 16 h. After reduction, the sample was flushed with inert gas for 30 min at 623 K. Afterwards, the flowing gas was replaced by a 5% H_2 in Ar flow and the sample was heated up to 1203 K (ramp: 10 K/min) while monitoring the H_2 consumption.

Hydrogen-static chemisorption was performed on the reduced catalysts in order to estimate the cobalt dispersion (D, %) and the cobalt crystallite size ($(dCo^0)_H$, nm)). The measurements were conducted in a ASAP 2020C unit at 308 K, after reducing approximately 0.15 g of the calcined catalyst at 623 K (ramp: 1 K/min) for 16 h. It was assumed that the adsorption stoichiometry is H:Co = 1 [22,23] and that the Pt does not contribute to the amount of H_2 adsorbed. The $d(Co^0)_H$ was estimated according to the following equation [24,25]:

$$d(Co^0)_H = \frac{96}{D} \cdot DOR \tag{1}$$

X-ray diffraction (XRD) was performed on the calcined catalyst using a Siemens D5000 diffractometer with Cu-Kα radiation ($2\theta = 10$–$90°$, step size = 0.02°) equipped with a Ni filter. The Co_3O_4 crystallite diameter ($d(Co_3O_4)_{XRD}$, nm) was estimated by using the Scherrer equation and assuming spherical crystallites (applying a correction factor of 4/3) [26]. The cobalt crystallite size ($(dCo^0)_{XRD}$,