Effect of H₂S in syngas on the Fischer–Tropsch synthesis performance of a precipitated iron catalyst

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Abstract

The sulfur limit, the relationship between the sulfur added and the surface Fe atoms lost (Fe/S), and mechanism of sulfur poisoning Fe catalyst were studied using an iron Fischer–Tropsch synthesis (FTS) catalyst (100 Fe/5.1 Si/2.0 Cu/3.0 K). The FTS reaction was carried out at 230–270 °C, 1.3MPa, H₂/CO = 0.67–0.77 and 30–70% CO conversion using a 1-L slurry phase reactor. The used Fe catalysts were characterized by XRD, Mössbauer spectroscopy and XANES spectroscopy to understand the deactivation mechanism of the Fe based catalyst after adding up to 1 ppm H₂S in the feed. Co-feeding of 0.1 ppm H₂S in syngas for 70 h changed very little the activity of the Fe catalyst, but increasing the H₂S level to 0.2 ppm or above resulted in measurable deactivation of the Fe catalyst over a similar time period. The limit of sulfur level in the syngas feed (sensitivity) was determined to be 50 ppb. Co-feeding of up to 1.0 ppm H₂S level was found to increase the extents of the secondary reaction of 1-olefins and the water gas shift (WGS) reaction even though the absolute rates were decreased with time. The addition of H₂S decreased CH₄ selectivity and increased C₅₊ selectivities of the Fe catalyst. The Fe/S ratio, which can be used to define the poison ability of sulfur for the iron catalyst, was quantified based on the deactivation data obtained. The Fe/S ratio strongly depended on temperature and decreased

remarkably with the increasing temperature. At 270 °C one sulfur atom was found to eliminate ~6 surface Fe atoms, and the ratio increased to 7.2 at 260 °C and increased further to 13.5 at 230 °C. The Fe/S relationship with increasing temperature is in good agreement with sulfur sorption theory. The changes in FTS and WGS rates of the Fe catalyst by sulfur were also studied. The decreases in rates of the two reactions were nearly the same. The results of XRD and Mössbauer spectroscopy indicated that the online addition of sulfur did not greatly alter the distributions of iron carbide and magnetite. Both data sets consistently suggest an adsorption mechanism, in line with the reaction results. XANES results at the S K-edge further confirmed sulfur adsorption, and some sulfide and sulfate species, likely confined to the surface zone, were detected. In this study, the sulfur tolerances of the precipitated Fe and a supported Co catalyst were compared at an identical temperature (i.e., 230 °C), and similar M/S ratios (13.5-15.0) were obtained.

Keywords: Fischer-Tropsch synthesis; Fe catalyst; XTL; slurry phase reactor, H₂S, Mössbauer spectroscopy, XANES, XRD

1. Introduction

Coal- or biomass-derived syngas generally contains a number of impurities such as sulfur compounds (e.g., H₂S and COS), halide compounds (e.g., NaCl and KCl), nitrogen-containing chemicals (e.g., NH₃, NO_x and HCN), traces of metals (e.g., Hg and Pb), and other compounds (e.g., NaHCO₃, KHCO₃, HCl, HF, and HBr) in addition to ash and tars [1-6]. These contaminants could behave as catalyst poisons when their concentrations in syngas reach specific limits; thus, they have the potential to significantly decrease catalyst activity and reduce catalyst life. For this reason, purification of syngas must be performed before it is introduced into the FTS reactor. From an economic perspective, gas purification is the most costly process in the

BTL technology, covering 65-70% of total cost [7]; identifying a potential poison's limit in syngas can significantly reduce gas purification costs by avoiding excessive gas-purification. In our most recent efforts, the effects of alkali halide and alkali bicarbonate compounds [8], ammonia [9], HCN [10], and hydrohalic acids (HX) i.e., HF, HCl, and HBr [11], on the catalytic behavior of an Fe catalyst (100Fe/5.1Si/2Cu/3K) have been extensively studied under commercially relevant FTS conditions. It was found that the tolerance levels of the catalyst to each of these poisons varied significantly. Ammonia, alkali halide and alkali bicarbonate compounds were found to be the weakest poisons to the Fe catalyst. When the level of ammonia in the syngas feed attained as high as 200 ppm [9] or when the concentrations of alkali halide and alkali bicarbonate compounds were less than 40 ppm [8], no significant changes in Fe catalyst performance were observed during 400 to 1200 h of continuous testing; instead, the HX limits were determined to be low, i.e. 1-2 ppm for HCl and HBr and 10 ppm for HF [11], indicating that the catalyst was much more susceptible to hydrohalic acids relative to ammonia and alkali compounds. In all cases, hydrocarbon selectivity was found to change very little at, or below, the lower limits of the poison effect, and a sorption mechanism was consistent with the findings, and deemed to be responsible for the deactivation.

The effect of sulfur compounds, such as H_2S and COS , on Co or Fe catalyst has been more frequently reported compared to nitrogen or halide containing compounds, but less so for Co catalysts [2,12-19]. Visconti et al. [18] studied the FTS performance of $\text{Co}/\text{Al}_2\text{O}_3$ catalysts when doping with 0–2000 ppm sulfur at 220 °C, 2.0 MPa and $\text{H}_2/\text{CO} = 2.0$ using a fixed-bed reactor. It was reported that sulfur decreased Co catalyst activity at all sulfur concentrations used but its impact on catalyst selectivity depended on sulfur level; low levels of sulfur (< 100 ppm) were found to have less of an effect on hydrocarbon selectivity, while high levels of sulfur (>100

ppm) decreased heavier hydrocarbon selectivity. Sparks et al. [17] recently conducted a sulfur poisoning study over a Co/Al₂O₃ catalyst at 220 °C, 2.0 MPa using a 1-L continuously stirred tank reactor (CSTR). A concentration of 0.75 ppm H₂S in the feed was reported to be a threshold limit to obtain noticeable cobalt catalyst deactivation; moreover, COS and CS₂ were found to more severely deactivate the cobalt catalyst relative to H₂S and deactivation by sulfur was reported to be based on a geometric site blocking model, with one sulfur atom being reported to eliminate six Co atoms [17]. Sulfur poisoning of Fe based catalysts for the FTS or the ammonia synthesis reaction was reported at the beginning of the 1920s according to Shultz et al. [12]. SO₂ was found to be the most severe poison for the reduced fused iron catalyst, while H₂S and ethyl mercaptan exhibited nearly the same effect [12]. All of the sulfur compounds tested (SO₂, COS, and H₂S) at the 10 mg S/g-Fe level decreased the activity of the Fe catalyst at 2.2 MPa and 240-300 °C, and at the same time decreased heavier hydrocarbon selectivity; this was ascribed to the formation of sulfur-promoter compounds. Anderson et al. [20] conducted a sulfur poisoning study over an iron catalyst by comparing the activity results under the syngas with or without H₂S using a fixed-bed reactor. The tests were conducted for long time periods (i.e., 56 to 100 days) at a constant temperature (260 °C) or a constant hydrocarbon yield (i.e., by evaluating temperatures from 260 to 390 °C) after the H₂S was introduced at a starting point where a steady state was first established. In the constant temperature experiment using 6.9-23 mg H₂S/m³ (4.8 – 14 ppmv), it was found that 80-100% of the S remained on carbide or reduced Fe catalyst; the catalyst activity decreased linearly with increasing sulfur concentration until 75% of the activity was lost. On the other hand, carbon deposition was presumed to be a primary cause of deactivation in the experiments conducted at constant hydrocarbon yields. Sulfur was reported to change very little the Fe catalyst selectivity. In the study of sulfur and carbon deactivation of

Al_2O_3 supported Fe, Co, Ni and Ru catalysts for the methanation reaction (conditions: 0.1 MPa and 390 °C) using a CSTR, 13-100 ppb of H_2S was reported to remarkably decrease the methanation rates of the Co/ Al_2O_3 and Fe/ Al_2O_3 catalysts; this was ascribed to site blocking on the catalyst surface. Each sulfur atom on the surface was reported to eliminate two surface Co or Fe atoms [16]. Bartholomew et al. [14] studied the effect of 0.6-6.0 ppm sulfur compounds on the activity and selectivity of unsupported and SiO_2 supported Fe catalysts with or without K and B promoters using a micro fixed-bed reactor (conditions: 227 °C, 0.1 MPa, and $\text{H}_2/\text{CO} = 2.0$). Addition of low levels of H_2S in syngas, i.e. < 2 ppm, led to faster deactivation of the iron catalyst compared to higher concentrations of H_2S , i.e. 5-6 ppm. The authors postulated that poisoning the catalyst with low levels of H_2S was due to physical blockage of metal sites by strongly adsorbed sulfur, while at the higher levels of sulfur, formation of a surface sulfide having a different structure or a multiple sulfide layer was responsible for the deactivation. The corresponding ratios of metal sites to sulfur (M/S) of 20 and less than 2-3 were determined at the low and high levels of sulfur conditions, respectively. The sulfur was not found to change the hydrocarbon distribution of the Fe catalyst in the study [14]. In addition to sulfur having been reported to deactivate the Fe catalyst, as summarized above, some studies reported an opposite effect on Fe catalysts. For example, sulfur concentrations up to 800 ppm (~1.3 mg S /g-Fe) were found in some cases to promote activity of the Fe catalyst under typical FTS conditions [15,21-23]. Reducing agent and promoter were also reported to affect the impact of sulfur on Fe catalyst behavior. H_2 and CO activated Fe catalysts were generally reported to tolerate different levels of sulfur, and metallic Fe was found to be more prone to form sulfide relative to iron carbide [23]. Promoters such as B, Mn and K were found to greatly improve the resistance of iron catalyst to H_2S poison, possibly serving as adsorbents for sulfur [14,22,23].

According to the above review, despite a number of sulfur studies (online or offline addition) performed on iron and cobalt based FTS catalysts, the conclusions of sulfur decreasing or increasing iron catalyst activity and sulfur decreasing or changing little the heavier hydrocarbon selectivity have been shown. The mechanism of sulfur poisoning of iron catalysts for FTS, as well as the ability of sulfur to poison iron (i.e., described as the relationship between the number of metal sites (in moles) affected by each mole of sulfur, have not, to date, reached a consensus (e.g., metal/S ratio varied over a wide range of 2-20). The reason for the difference is not well understood, but it could be associated with different sulfur concentrations and/or process conditions used. Furthermore, the sensitivity of iron and cobalt based catalysts to sulfur, which can be described by an upper limit of sulfur in the feed, was not systemically studied. Finally, most of the previous sulfur effect studies on iron and cobalt FTS catalysts were performed using a fixed-bed reactor, where gradients of sulfur and reactant concentrations along the catalyst bed existed; moreover, the testing periods in most studies were relatively short (usually less than <150 h).

Because of the quite complicated and controversial effects of sulfur reported previously (i.e., impact on activity, selectivity, sulfur limit and Fe/S value), it is important to further study these sulfur-related issues using a CSTR reactor, such that deeper insights into the impact of sulfur on typical Fe FTS catalysts can be assessed. The FTS reaction was conducted at three different temperatures i.e. 230, 260 and 270 °C by continuously co-feeding H₂S for several hundred hours in order to obtain representative catalyst deactivation information resulting from the contaminant addition. This allows the effect of temperature on the impact of sulfur on Fe catalyst behavior to be examined, reports of which are lacking. The limit of H₂S was determined by progressively increasing the H₂S level from 100 ppb to 1.0 ppm. The Fe/S ratio was

determined using noticeable catalyst deactivation data resulting from specific poisoning levels (i.e., 1 ppm H₂S) in order to minimize measurement error. To compare the ability of sulfur to poison iron and cobalt catalysts, an identical temperature, 230 °C, was used. In addition, all used catalysts, after washing with hot o-xylene, were characterized by XRD, Mössbauer spectroscopy, and XANES spectroscopy such that the deactivation mechanism on the Fe catalysts resulting from the co-fed sulfur could be evaluated.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1 Iron catalyst preparation

Details of the iron catalyst preparation can be found elsewhere [6,24]. In brief, a base Fe catalyst 100 Fe/5.1 Si/1.25 K was first prepared using a precipitation method. The 100 Fe/ 5.1 Si/ 3.0 K/ 2.0 Cu catalyst used in this study was prepared by sequential impregnation of an appropriate amount of K (KNO₃, 99.9 % purity) and Cu (Cu(NO₃)₂·2.5 H₂O, 99.9 % purity) containing solutions onto the base catalyst. Between each step, the catalyst was dried under vacuum in a rotary evaporator at 80 °C and the temperature was slowly increased to 95 °C. After the second impregnation/drying step, the catalyst was calcined under air flow at 350 °C for 4 h. The BET surface area, BJH pore volume and pore diameter are 107 m²/g, 0.154 cm³/g-cat and 6 nm, respectively [6,8].

2.1.2 Cobalt catalyst preparation

The 0.5%Pt-25%Co/Al₂O₃ used in this study was prepared using a slurry phase impregnation method. The catalyst support was Sasol Catalox-150 γ -Al₂O₃. Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) (Alfa Aesar) was employed to make the Co precursor solution.

Two impregnation steps of cobalt nitrate were applied. Between each step the catalyst was dried under vacuum in a rotary evaporator. After the last step of cobalt addition, platinum precursor solution (Tetra-amine platinum (II) nitrate) was added to the Co/Al₂O₃ catalyst by incipient wetness impregnation. Only after the final step were catalysts calcined under air flow at 350 °C for 4 h. More detailed preparation procedures can be found elsewhere [6].

2.1.3 XRD measurements

To identify Fe carbides/oxides and, potentially, Fe-sulfur compounds formed by reaction with H₂S, powder X-ray diffraction (XRD) analysis of the used catalysts was carried out at room temperature using a Panalytical X'Pert Diffractometer (PW-3040 PRO) operating with Cu K α radiation (1.54 Å). Before the XRD experiment, the used catalyst sample was extracted using hot o-xylene.

2.1.4 Mössbauer spectroscopy measurements of the iron catalyst

Mössbauer spectroscopy measurements were conducted in transmission mode, with the ⁵⁷Fe source mounted in a standard constant acceleration velocity transducer. The Fe samples in slurry form, which were collected at different times during a run or the end-of-run, were placed in a copper holder, and were mounted near the finger of a vibration-free closed-cycle refrigerator which provided temperatures as low as 20 K. Structural analysis of the sample was performed by least-squares fitting of the Mössbauer spectra to a summation of hyperfine sextets. The least squares fitting procedure employed user-defined functions within the Peak Fit program. The parameters for each sextet in the fit consisted of the position, width and height of the first peak, the hyperfine magnetic field, and the quadrupole electric field. These parameters were allowed to vary freely to obtain the best fit of the experimental data. Errors in the determined percentages of Fe values are about ± 3 % for well-resolved spectra; in those that contain several iron oxide and

carbide phases, the uncertainty increases with the complexity of the spectrum (i.e., depending on the degree of overlap and the weakness of the signal).

2.1.5. XANES measurement of used iron catalyst

The electronic structure of sulfur and iron following catalyst poisoning was investigated by XANES in fluorescence mode near the S K-edge and Fe K-edge at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source, Inc. The used catalyst sample, after H₂S poisoning in a CSTR under realistic Fischer-Tropsch synthesis conditions, was sealed in the wax product for analysis by comparison with reference compounds of interest. The spectra (in energy space) were background subtracted and normalized with a two-polynomial method with degree 1 for both the pre- and post-edge regions using the WinXAS [25] software.

2.2 Fischer-Tropsch synthesis reaction

The 100Fe/ 5.1Si/ 3.0K/ 2.0 Cu catalyst was activated in-situ using a CSTR, and the following conditions were used: 270 °C, 0.1 MPa, and 2.0 NL/g-cat/h CO for 24 h. The catalyst poisoning study was carried out using a 1-L CSTR under the conditions: 230-270 °C, 1.3 MPa, 10.0 NL/g-cat/h, and H₂/CO ratio of 0.67-0.77. H₂S in H₂ or N₂ with a concentration between 5 and 20 ppm was co-fed with syngas to provide 0.1-1.0 ppm H₂S in the feed when the catalyst steady state was established, which usually took between 90 and 120 h. To effectively compare the sensitivity of Fe and Co catalysts to poisoning by H₂S, a test run with a Co based catalyst was conducted by co-feeding 0.3 to 1 ppm H₂S. Changes in CO conversion, selectivities to CH₄ and C₅₊ (carbon atom basis), C₄ olefin selectivity (100 x (rate of all C₄ alkenes)/(rate of all C₄ alkenes + rate of all C₄ alkanes)) and 1-C₄ olefin selectivity (100 x (rate of 1-C₄ alkenes)/(rate of all C₄ alkenes)) as functions of time and contaminant concentration were used to evaluate the impacts of the H₂S.

3. RESULTS AND DISCUSSION

3.1 Effect of H₂S on an iron Fischer-Tropsch synthesis catalyst

The sensitivity of the Fe-K catalyst to H₂S was first tested at 260 and 270 °C in two different runs. At 270 °C, co-feeding 1.0 ppm H₂S lasted for 190 h from a steady state point that was established at ca. 120 h. In the test run at 260 °C, two H₂S concentrations, 0.3 and 1.0 ppm H₂S in syngas, were examined for 311 h, starting from a stable CO conversion of 66%. The syngas pressure was maintained at a constant value of 1.3 MPa over the entire testing period. The effect of H₂S on FTS activity is shown in Figure 1.

Figure 1 indicates that the Fe catalyst is very sensitive to the H₂S poison. Adding 0.3 or 1.0 ppm H₂S resulted in slow or pronounced deactivation. At 270 °C, CO conversion remained at 72.8% without addition of the sulfur before 145 h. After 1.0 ppm H₂S was introduced at this point, CO conversion declined rapidly and it was only 49.8% when the H₂S gas was terminated at 311 h. The percentage of the activity decrease was 31.6% in the 165 h of co-feeding of the poison, which is equivalent to 4.55% of loss in CO conversion ($Y = 100 \times (X_{CO,t0} - X_{CO,t}) / X_{CO,t0} / (t - t_0) \times 24$) per day. At 260 °C, the addition of 0.3 ppm H₂S was first performed between 167 h and 311 h, which led to a slow decrease in CO conversion from 67.4% to 62%. However, in a similar manner to the results at 270 °C, when a higher level, i.e. 1.0 ppm, of H₂S was introduced at this lower temperature between 311 and 479 h, rapid deactivation happened again at the lower temperature. This resulted in CO conversion being decreased further to 29%, representing a 53.7% decrease in 168 h. The hydrocarbon selectivity results at different times and different H₂S levels are discussed below.

One of the important tasks of this study is to identify the upper limit of H₂S (Fe catalyst sensitivity) in the feed gas, which is the concentration that the Fe catalyst can tolerate under industrially relevant conditions. Consequently, a temperature of 270 °C was selected to investigate the limit of H₂S for the Fe catalyst. The level of H₂S in syngas was progressively increased with small intervals, i.e. 0.1, 0.2, 0.3, 0.5 ppmv using 19 ppmv H₂S in N₂ gas mixture. The duration of the poisoning test was ca. 400 h. The results, included activity, selectivities to CH₄, C₅+, CO₂ and total C₄ olefin and 1-C₄ olefin, are presented in Figure 2 a-d.

Figure 2a shows that cofeeding 0.1 ppm H₂S for 96 h (120-216) led to a small drop in CO conversion from 79.7 to 78.8%. Following testing at this low level, the H₂S level in the feed was gradually increased to 0.2, 0.3 and 0.5 ppm at 216, 312, 392 h, respectively; this resulted in a notable decrease in CO conversion at all of the H₂S levels. It was seen that CO conversion decreased 1.8% (78.8 to 77%) during testing with 0.2 ppm H₂S for 98 h, while the decreases in CO conversion increased remarkably to 3.2% (77 to 73.8%) and 12.2% (73.8 to 65.6%) when higher H₂S levels, i.e. 0.3 and 0.5 ppm, were tested for a similar time period. Thus, the deactivation rate increased significantly with increases in the H₂S level. The value of the slope for each deactivation line shown in Fig 2a became more negative (-0.0023 for 0.1 ppm H₂S, -0.0031 for 0.2 ppm H₂S, -0.0168 for 0.3 ppm H₂S and -0.0669 for 0.5 ppm H₂S) with increases in the H₂S level, consistent with an increased deactivation rate. At 511 h, the H₂S/N₂ gas mixture was switched off in order to establish a new steady state for testing at a lower temperature.

Based on the above results, as shown in Figures 1a and 2a, 0.1 ppm H₂S in syngas is very close to the upper limit for the Fe catalyst at 270 °C. To more accurately define the value, calculation of the percentage loss in CO conversion per day at each H₂S level (X = 0.1, 0.2, 0.3, 0.5 and 1.0 ppm) was performed, and the results are shown in Figure 3. Surprisingly, the

percentage loss in CO conversion per day increased linearly with increases in the H₂S level; for example, they were 0.28%, 0.57%, 1.25%, 2.24% and 4.55% as the H₂S level increased over the series 0.1, 0.2, 0.3, 0.5 and finally 1.0 ppm, respectively. The r-squared linear correlation coefficient (R^2) value for the regression of Y and X approaches unity (0.998), further indicating the highly linear relationship between the two parameters. In term of this good linear regression line, extrapolating the plot to zero deactivation, 50 ppb H₂S in the syngas feed was determined to be the upper limit for the Fe based catalyst used under the FTS conditions.

The effect of sulfur on various hydrocarbon selectivities is another interesting topic that has not been widely reported. Figure 2b-d shows the changes in the selectivities of CH₄, C₅₊, CO₂, 1-C₄ olefin, 2-C₄ olefin and C₄ paraffin with time on stream. Before co-feeding H₂S, CH₄ and C₅₊ selectivities stabilized at 3.9% and 79.2%, respectively. Interestingly, upon introducing 0.1 ppm H₂S, CH₄ selectivity slowly decreased and C₅₊ selectivity gradually increased with time. When the H₂S/H₂ gas mixture flow was stopped at 511 h, CH₄ selectivity had decreased to 3.3% and C₅₊ selectivity had increased to 80.7%. The decrease in CH₄ selectivity during feeding 0.1-0.5 ppm H₂S was likely due to the competitive adsorption between sulfur and hydrogen on the iron catalyst surface (to be discussed). CO₂ selectivity is defined by the WGS rate to the total rates of FTS and WGS. Even though both the WGS rate and the FTS rate declined during deactivation by sulfur (results not shown); however, the declines differed slightly so that the CO₂ selectivity slightly increased (45.8-46.8%) with time. Furthermore, adding up to 0.5 ppm H₂S had only a slight effect on olefin and paraffin selectivities. Considering the fact that decreasing CO conversion generally lowers the WGS activity and secondary reactions of olefins for Fe and Co catalysts [26,27], the slight increases in CO₂ and 2-C₄ olefin selectivities (Figs 2b-d)

observed during testing of the H₂S poison suggests that the added sulfur modified (e.g., improved) the extents of WGS reaction and secondary reaction of olefins.

In the FTS reaction on the iron catalyst, the water gas shift reaction adjusted hydrogen concentration; thus, the H₂/CO ratio in the reactor is one variable responsible for altering hydrocarbon selectivity. In the absence of H₂S poisoning, CO₂ selectivity was observed to decrease, i.e. from 48 to 45% with decreases in CO conversion, which reduced the H₂/CO ratio during FTS (Figure 4). This resulted in corresponding decreases in CH₄ selectivity (i.e., 3.8 to 2.8%, or 6.5 to 5.5%) and increases in C₅₊ selectivity (i.e., 82 to 84%, or 72 to 75%) with decreases in CO conversion (i.e., from 80 to 50%) by adjusting contact time for Fe catalysts promoted with 1.2 or 3% potassium [26]. The current CH₄ and C₅₊ selectivity trends observed when 0.1-1.0 ppm H₂S were co-fed are the same as those obtained with the decreases in CO conversion, but without H₂S even though the changes were not very great (Figure 2b). However, the cause cannot be ascribed to the adjustment of the WGS reaction instead of H₂S itself. It was noted that the CO₂ selectivity was enhanced during the addition of H₂S (Fig 2 b), which is different from the case with the decreases in CO conversion by adjusting contact time without sulfur addition. The increased CO₂ selectivity by H₂S must bring about an increased exit H₂/CO ratio and thus should tend to increase CH₄ selectivity with deactivation. However, the actual CH₄ selectivity instead decreased slowly with deactivation by H₂S. This firmly suggests that the added sulfur played a role in adjusting CH₄ formation, probably through competitive adsorption of sulfur and hydrogen on the Fe catalyst surface. The decrease in CH₄ and the increase in C₅₊ (corresponding to lower H₂/CO usage ratio) with the deactivation consequently yielded a decreased exit H₂/CO ratio trend (Figure 4).

The decreases in CH₄ selectivity and increases in C₅₊ selectivity with the addition of H₂S as shown in Figure 2 b were not observed in studies from the open literature when H₂S was added online with the syngas feed. However, it was reported for an iron Fe catalyst that was pre-dosed with 800-1500 ppm sulfur [22]. The authors proposed that the formation of a Fe-S compound during calcination was responsible for the selectivity change. Others have observed little changes in the selectivities to CH₄ and C₅₊ of Fe catalysts by the online addition of H₂S [14,18,20]. Some investigators have reported that sulfur decreases heavier hydrocarbon selectivity [12,18], or increases olefin and 2-olefin contents in the hydrocarbon products [22,23,28]. The discrepancies regarding the sulfur effect on hydrocarbon selectivity between this study and previous studies is not well understood. The different sulfur levels or different process conditions used could be responsible for the different selectivity results.

In this study, 50 ppb H₂S in the syngas was found to be an upper limit at 270 °C. Fischer [29] first reported that an upper limit of sulfur concentration of 1-2 ppm in syngas for fused Fe based FTS catalysts. Dry [30] suggested that the sulfur content of syngas should be kept lower than 20 ppb for the minimization of the deactivation of iron and cobalt industrial FTS catalysts. Recently, Sparks et al. [17] reported that 0.75 ppm H₂S was a threshold concentration for a cobalt catalyst that led to noticeable catalyst deactivation. Thus, the H₂S limit for the Fe catalyst determined in the current study is close to or slightly higher than the value proposed by Dry. The slightly higher sulfur limit determined may allow for a simplification of the syngas purification process and an improvement of the economics of the XTL process.

To determine the effect of temperature on the relationship between surface Fe and sulfur atoms as discussed below, the temperature of the run (after testing 0.1-0.5 ppm H₂S had been completed at a time on-stream of 511 h) was decreased to 230 °C, and CO conversion was

adjusted to about 42% between 511 and 577 h as a new steady state. A concentration of 1.0 ppm H₂S was subsequently added at 577 h and maintained at that level for another 216 h. The change in CO conversion with time is shown in Figure 5. It was observed that CO conversion decreased from 42 to 28.7% when 1.0 ppm H₂S was suspended at 793 h. Thus, the mean percentage of loss in CO conversion per day was 3.53%. The selectivities to various species in the deactivation period were similar to the results shown in Figure 2. For the sake of brevity, the selectivity results are not included.

3.2 Determination of the relationship between surface iron and sulfur (Fe/S)

An adsorptive (e.g., site blocking) deactivation mechanism was proposed to be primarily responsible for H₂S poisoning of the Fe catalyst based on the reaction results as discussed above and the results of XRD, Mössbauer spectroscopy, and XANES results as discussed below (Section 3.4). Assuming that all sulfur that was introduced was taken up by the Fe catalyst surface, and assuming that surface iron (e.g., iron carbide) sites were responsible for catalyst activity, the relationship between the amount of surface iron atoms lost during deactivation and the amount of sulfur atom introduced (Fe/S) at each temperature could be estimated. As such, the impact of temperature on the Fe/S ratio over the Fe catalyst could also be determined. Since the surface active sites of the iron phases are assumed to be responsible for the disappearance rate of CO, the percentage losses in surface Fe active sites must be proportional to the percentage decrease in the CO rate. The number of surface iron atoms per gram of catalyst was estimated using the catalyst surface area and the Fe catalyst density of $9.4 \times 10^{-20} \text{ m}^2/\text{Fe}$ [29]. To avoid large experimental errors occurring when calculating Fe/S ratios, only the pronounced

deactivation rates resulting from the high H₂S level of 1.0 ppm were used to determine the Fe/S ratio. The Fe/S ratios at 270, 260 and 230 °C are shown in Figure 6.

Figure 6 demonstrates that the surface Fe atoms lost and the corresponding sulfur atoms introduced exhibit good linear relationships at each temperature, as indicated by the high correlation coefficients ($R^2 > 0.96$). Interestingly, the Fe/S ratios determined by the slopes of the lines increased with decreases in temperatures, i.e. 13.5 at 230 °C, 7.2 at 260 °C and 5.9 at 270 °C, which suggests that the sulfur poisoning strength was weakened at higher temperatures. The results in turn suggest that the proposed adsorption and site blocking mechanism very likely accounted for the observed deactivation.

Bartholomew et al. [14] studied the Fe/S ratios on SiO₂ supported Fe FTS catalysts at 227 °C and atmospheric pressure using 0.5-6 ppm H₂S. They reported that the Fe/S ratio was in the range of 10-20 in the low range of sulfur concentration, i.e. 0.5-2.0 ppm. The Fe/S ratio obtained in this study at 230 °C, 13.5, apparently falls into the range reported by Bartholomew et al. In a methanation reaction study over supported Fe, Co, Ni catalysts [16], it was reported that 0.013-0.1 ppm sulfur was found to deactivate the Fe catalyst tested at a higher temperature of 390 °C based on a metal/S ratio of 2.0. The low Fe/S ratio reported at this high temperature was indeed in line with the results achieved in this study, i.e., the ability of sulfur to poison the catalyst was lower at higher temperature. The changes in the Fe/S ratio with temperature based on the results of this study, as well as those from the open literature, are summarized in Figure 7.

3.3. XRD results of used Fe catalysts

To understand the deactivation mechanism by sulfur in this study, XRD results of the used catalysts that were exposed to 1.0 ppm H₂S at 270 °C and 260 °C, as well as clean

conditions (i.e., no H₂S) are provided in Figure 8. Fe₃O₄ and Fe₅C₂ phases were detected at 2θ of 30°, 35.5° and 40°, 42.6°, 45.0° and 50.5° respectively, which were also observed on the Fe catalysts exposed to ammonia [9]. Iron-sulfur compounds with sufficient long range order were not detected by XRD, and the distributions of iron carbides and magnetite did not change significantly after sulfur poisoning. These results indicate that the interaction between Fe and S was on the scale of short range order; thus, the accelerated deactivation of the Fe catalyst with co-fed sulfur was presumed to be due to sulfur blocking of active sites (e.g., Fe carbide). This proposed deactivation mechanism is consistent with the results of Mössbauer spectroscopy discussed below and can explain the unchanged hydrocarbon selectivities (i.e., taking into consideration the CO conversion effect on selectivity) obtained during testing of various levels of H₂S. These conclusions are in line with the literature, which focused on investigating 0.5-6.0 ppm H₂S on Co/SiO₂ and Fe/SiO₂ catalysts [14], and in which the site blocking by sulfur was reported to be a predominant deactivation mechanism at sulfur levels less than 2.0 ppm.

3.4 Mössbauer spectroscopy results

Mössbauer spectra of the four Fe samples collected at the end of runs without and with 1 ppm H₂S conditions at 270 and 260 °C are shown in Figure 9. Three phases of iron, i.e. χ -Fe₅C₂, ϵ' -carbide, and magnetite (Fe₃O₄), were detected in all samples, which are represented by three blue sextets, two green sextets and one red sextet, respectively. Interestingly, the intensity of three iron phases in the Fe samples at the end of run – either with or without sulfur poisoning with 1 ppm H₂S at 270 °C - are quite similar; the composition was 42-47% magnetite, 15% ϵ' -Fe_{2.2}C and 32-39% and χ -Fe₅C₂ (Table 1). However, at 260 °C the intensity of red lines and blue lines decreased and that of the green line increased significantly (Figure 9). As shown in Table 1,

the amounts of magnetite and χ -Fe₅C₂ decreased to 29% and 32%, respectively, and the amount of ϵ -Fe_{2.2}C increased to 32%. The results of Mössbauer spectroscopy reflect three important aspects about the behavior of sulfur: 1) χ -Fe₅C₂ phases were unstable at low temperature conditions, and a fraction of them converted to ϵ -Fe_{2.2}C; 2) the formation of bulk Fe-S compounds as a deactivation mechanism in the current context was ruled out, consistent with the results of XRD; 3) co-feeding sulfur for several hundreds of hours did not alter the distribution of the iron phase, indicating that sulfur adsorbed on iron sites in a uniform manner.

ϵ -Fe_{2.2}C and χ -Fe₅C₂ exhibited better stability at low and high temperatures, respectively, which is consistent with our earlier study [9] and that of a study in the open literature [31]. The lower amounts of iron magnetite found in the used sample at 260 °C relative to the one at 270 °C could be ascribed to a lower extent of oxidation of χ -Fe₅C₂ by water ($3\text{Fe}_5\text{C}_2 + 32\text{H}_2\text{O} = 5\text{Fe}_3\text{O}_4 + 6\text{CO}_2 + 32\text{H}_2$).

3.5 XANES spectroscopy results

The XANES spectrum of the catalyst at the Fe K-edge is shown in Figure 10. The lower energy XANES feature indicative of reduced Fe in Fe carbide appears as a shoulder at ~7.112 keV, and its intensity lies between that of the Fe⁰ reference compound and that of Fe₃O₄ oxide, and is consistent with typical spectra of carburized Fe catalysts that contain a fraction of residual Fe₃O₄. The feature for Fe in a higher oxidation state is characterized by the white line intensity, and once again, the catalyst white line intensity is between that of the Fe⁰ reference and Fe₃O₄. Fully carburized references, not shown, typically exhibit a broad low intensity white line. Because sulfur poisoning was confined to the surface and the catalyst contains significant Fe content, no obvious features associated with S poisoning were observed at the Fe K-edge.

However, analysis at the S K-edge, as shown in Figure 10, reveals that S is indeed present on the catalyst following H₂S poisoning. At least three pronounced features in XANES were detected, including two low energy features between ~2.47 and 2.473 keV, and a higher energy peak at 2.477 and 2.484 keV. By comparison with the reference spectra for Fe sulfides, as well as Fe and K sulfates, the low energy features are likely associated with surface Fe sulfide species, presumably adsorbed on the reduced Fe carbidic phase. The higher energy feature resembles that of a sulfate surface complex (or related compound). It is likely associated with S adsorption on the oxidic Fe phase and /or the promoter (i.e., K, Cu, or both).

Because the technique is not confined to the surface (i.e., it averages over surface, subsurface, and bulk), and because no significant changes in Fe electronic structure were detected by XANES at the Fe K-edge, the results suggest that bulk Fe-S compounds did not form to a significant extent. This is in agreement with results from XRD and Mössbauer spectroscopy. No Fe-S compounds with sufficient long range order were observed by XRD. However, XANES is not limited by long range order. Thus, the S species detected by XANES at the S K-edge were likely confined to the surface zone, and could be responsible for site blocking of Fe on the surface of the catalyst.

3.6 Effect of H₂S on the FTS and WGS rates

Table 2 summarizes the FTS and WGS rates and their loss percentages during co-feeding of 1 ppm H₂S at 260 and 270 °C. For a comparison, the WGS rates, FTS rates and the ratios of loss percentage of the WGS rate to that of the FTS rate for the Fe catalyst poisoned by halogen ions (F, Cl and Br) are also listed in Table 2. Interestingly, The ratios of loss percentage of the WGS rate to that of FTS in all sulfur test runs are close to 1.0 (1.1), but in the case of halogen

ions (F, Cl and Br), the ratios of loss percentage of the WGS rate to that of FTS all increased to 1.42-1.86, which means a greater impact on the WGS rate than the FTS rate by the halogen ions. The results suggest that poisoning of iron FTS catalysts by sulfur and halogen ions is quite complicated. The current results indicate that the sulfur effect on the changes in the rates of FTS and WGS differed from that of the effect of halogen ions, even though adsorption was assumed to be the deactivation mechanism in both cases. It could be that sulfur adsorbed in a more uniform manner on FTS and WGS sites than the halides, resulting in the ratio being closer to unity. Additional studies are needed to further elucidate the complicated issue of how the poisons impacted the relative FTS and WGS rates of the Fe catalysts.

3.7 Comparison of the effect of H₂S on Co and Fe catalysts

The effects of sulfur on Fe and Co based catalysts has been studied by many investigators; however, the issue as to which catalyst is more sensitive to poisoning by sulfur is not well defined. To shed light on this, a test run with a 0.5%Pt-25%Co/Al₂O₃ was conducted at 220 and 230 °C and 2.0 MPa, such that sulfur poisoning could be compared at the same temperature (i.e., 230 °C). The change in CO conversion with time, as well as the effect of temperature, under steady state conditions and co-feeding 1 ppm sulfur, are summarized in Figure 11. In two separate tests (220 and 230°C), steady states was established for 100 h prior to addition of 0.3-1.0 ppm H₂S for several hundreds of hours. It was found that the cobalt catalyst displayed distinctive deactivation at 220 °C when 0.3 ppm H₂S in feed was used, where CO conversion decreased by 14.8% in 118 h. This means that the average percentage of loss in CO conversion per day was 6.3%. Increasing the H₂S level to 1.0 ppm at 230 °C markedly increased the catalyst deactivation rate, with the loss in CO conversion points being 18.6% within 73.4 h which was a

higher mean percentage of loss in CO conversion per day, 12.4%. Based on the sulfur deactivation data at 220 and 230 °C, the relationship between the surface cobalt atoms and moles of sulfur entering the reactor was determined and plotted in Figure 12. The Co/S ratio was calculated to be 31.1 and 15.0 at 220 and 230 °C, respectively.

Comparing the Fe/S ratio and Co/S ratio obtained at 230 °C, the sulfur poisoning of cobalt and iron appear to be similar, or perhaps slightly higher with cobalt. However, the Fe catalyst may be more sensitive to sulfur than cobalt since the threshold of H₂S for the Fe catalyst was found to be lower.

The Co/S ratio at 220 °C was determined to be 31 in this study (Fig 12), which is significantly greater than the value of 6.0 reported previously [17]. It is speculated that the different results could be due to the cobalt catalyst having been partially deactivated (e.g., by oxidation) before measuring the sulfur effect in the previous study. That is, the most sensitive sites (i.e., the higher energy sites) may have already been suppressed prior to sulfur poisoning in the previous study.

4. Conclusions

The effects of H₂S on the activity and selectivity of a 100 Fe/5.1 Si/2 Cu/3 K catalyst were studied using a 1 L CSTR at 230-270 °C, H₂/CO = 0.67-0.77, 1.5 MPa and CO conversion levels in the range of 30-80%. The freshly activated and used Fe catalysts were characterized by XRD, Mössbauer spectroscopy, and XANES spectroscopy to shed light on the mechanism of poisoning of the Fe catalyst during co-feeding of H₂S for several hundreds of hours. The sensitivity of 100 Fe/5.1 Si/2 Cu/3 K catalyst to the H₂S poison and the impact of sulfur on Fe catalyst sites were defined by the sulfur limit and the Fe/S ratio, respectively, which were

quantified. The characterization results highlighted a deactivation mechanism involving the adsorption of sulfur, in line with the FTS reaction results.

Continuous co-feeding of 0.1, 0.2, 0.3, 0.5 or 1.0 ppm H₂S in the syngas to CSTR for 72-150 hours resulted in different deactivation rates (DR). Adding 0.1 ppm H₂S for 72 h led to a small deactivation, for example, the DR based on average percentage loss in CO rate per day at 270 °C was 0.28%; increasing the H₂S level from 0.2 to 1.0 ppm linearly increased the DR from 0.57 to 4.6%. The H₂S limit for the iron catalyst at which nearly zero deactivation rate can be achieved was determined to be 50 ppb. The co-feeding of different levels of H₂S altered the product selectivities. Adding sulfur for about 400 h was found to gradually decrease CH₄ selectivity and increase C₅₊ selectivity. The added sulfur improved extents of the secondary reaction of olefins and the WGS reaction even though the absolute rates were declined.

The Fe/S relationship and the effect of temperature on the Fe/S ratio was successfully determined. In line with the sorption theory, the Fe/S ratio decreased dramatically from 13.5 to 6.0 when the temperature was increased from 230 to 270 °C. The results suggest that sulfur poisoning of the Fe catalyst was exacerbated at lower temperatures.

Sulfur resulted in nearly the same % of loss in the WGS rate and FTS rate of the iron catalyst. In contrast, the halides (F, Cl, Br) led to much higher loss % of the WGS rate relative to that of the FTS rate. It was postulated that sulfur could be adsorbed on the FTS and WGS sites of the iron catalysts in a more uniform manner than the halides.

The deactivation of the Fe catalyst by H₂S was proposed to occur mainly through a site blocking mechanism by sulfur blocking on iron sites. XRD, Mössbauer results, and XANES results at the Fe K-edge confirmed that no significant bulk Fe-S compounds were formed. However, analysis of XANES data at the K-edge of S suggested that S adsorbed on the surface

of the Fe catalyst to form surface sulfide and sulfate species. These may be responsible for the site blocking mechanism. A comparison of the ability of H₂S to poison the Fe catalyst and a typical Co catalyst was made. At 230 °C, the number of metal atoms lost per mole of sulfur adsorbed was similar for the Fe and Co catalysts (13.5-15.0).

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Figure Captions

- Figure 1.** Effect of 0.3-1 ppm H₂S on CO conversion over 100Fe/5.1Si/3K/2Cu. FTS conditions: 270 °C, 1.3 psig (CO+H₂), H₂/CO = 0.77, SV_{CO+H₂}=10 NL/g-cat/h and 260 °C, 1.3 MPa (CO+H₂), H₂/CO = 0.67, SV_{CO+H₂}=10 NL/g-cat/h.
- Figure 2.** Effect of 0.1-0.5 ppm H₂S on (a) CO conversion, (b) CH₄, (c) C₅₊, (d) CO₂, (e) 1-C₄ olefin, (f) 2-C₄ olefin, (g) t-C₄ olefin (h) C₄ paraffin selectivities over 100Fe/5.1Si/3K/2Cu. FTS conditions: 270 °C, 1.3 psig (CO+H₂), H₂/CO = 0.77, SV_{CO+H₂}=10 NL/g-cat/h and 260 °C, 1.3 MPa (CO+H₂), H₂/CO = 0.67, SV_{CO+H₂}=10 NL/g-cat/h.
- Figure 3.** Relationship between CO conversion decrease percentage and H₂S level used on 100Fe/5.1Si/3K/2Cu catalyst. FTS conditions: 270 °C, 1.3 psig (CO+H₂), H₂/CO = 0.77, SV_{CO+H₂}=10 NL/g-cat/h.
- Figure 4.** Change in exit H₂/CO ratio with CO conversion by H₂S deactivation (270 °C, H₂/CO = 0.77 and 1.3 MPa) or by adjusting contact time without deactivation (260 °C, H₂/CO = 0.67 and 1.3 MPa).
- Figure 5.** Effect of 1 ppm H₂S on CO conversion over 100Fe/5.1Si/3K/2Cu. FTS conditions: 230 °C, 1.3 psig (CO+H₂), H₂/CO = 0.77, SV_{CO+H₂}=3.0 NL/g-cat/h.
- Figure 6.** Relationships between the amounts of surface iron lost and the amounts of sulfur introduced at different temperatures.
- Figure 7.** Change in deactivation stoichiometry for the loss of surface Fe atoms per sulfur atom sorbed (H₂S < 1.0 ppm) with temperature.

- Figure 8.** XRD spectra of used Fe-K catalyst after exposing to 1.0 ppm H₂S at (top) 260 °C, (middle) 270 °C, and (bottom) without H₂S poisoning.
- Figure 9.** Mössbauer spectra of the Fe catalysts (a) after H₂S poisoning at 260 °C, (c) after H₂S poisoning at 270 °C. Blue sextets alone correspond to Hägg carbide; green sextet G2 alone corresponds to ϵ -Fe_{2.2}C; red sextets alone correspond to magnetite.
- Figure 10.** XANES spectra of the H₂S poisoned used Fe catalyst in comparison with the spectra of reference compounds taken in fluorescence mode at the K edges of (left) Fe and (right) S.
- Figure 11.** Effect of time, temperature and up to 1.0 ppm H₂S on CO conversion on 0.5%Pt-25%Co/Al₂O₃. Other FTS conditions: 2.0 MPa(CO+H₂), H₂/CO = 2.0, SV_{CO+H₂} = 3.2 NI/g-cat/h.
- Figure 12.** Relationships between the amounts of surface cobalt lost and the amounts of sulfur introduced at different temperatures.

Table 1. Results of Mössbauer spectroscopy least-squares fitting of the Fe catalysts before and after co-feeding H₂S (G1 and G2 stand for the green sextets while B1, B2 and B3 stand for the blue signals in Figures 9a-b).

Poison/TOS, h	Temperature, °C	Iron phases			Details of iron carbides					Summary of iron Carbides	
		Fe% in Magnetite	Fe% in Carbides	Fe%	Fe% in G1	Fe% in B1	Fe% in B2	Fe% in G2	Fe% in B3	G1+G2 (ε'-Fe _{2.2} C)	B1+B2+B3 (χ'-Fe ₅ C ₂)
Baseline run without H ₂ S/336	270	47	53	0.0	5.0	17.0	10.0	9.0	12.0	14.0	39.0
1.0 ppm H ₂ S/599	270	42	53	5.0	6.0	6.0	10.0	9.0	13.0	15.0	39.0
1.0 ppm H ₂ S/478	260	29	67	4.0	13.0	14.0	8.0	21.0	10.0	34.0	32.0

Table 2. Summary of WGS rate, FTS rate and their percentage losses using the Fe catalyst during co-feeding of 1 ppm H₂S and ~20 ppm hydrohalic acids

Poison and level	Temperature, °C	Time, h	r _{WGS} , mol/g _{cat} /h	r _{FTS} , mol/g _{cat} /h	WGS rate loss %	FTS rate loss%	Ratio of WGS rate loss% / FTS rate loss%
30 ppm HF*	270	553	0.0812	0.0973	57.6	34.2	1.68
		673	0.0344	0.0640			
40 ppm HCl*	270	240	0.0901	0.0948	88.4	57	1.55
		432	0.0104	0.0407			
40 ppm HBr*	270	432	0.0575	0.0727	55.1	29.6	1.86
		562	0.0258	0.0512			
20 ppm HF*	260	411	0.0746	0.0868	73.2	44.6	1.64
		719	0.0200	0.0481			
23 ppm HCl*	260	954	0.0252	0.0362	81.0	51.7	1.57
		1100	0.0048	0.0175			
20 ppm HBr*	260	920	0.0515	0.0666	73.7	51.8	1.42
		1178	0.0153	0.0321			
1 ppm H ₂ S	270	197	0.0747	0.0851	32	29.0	1.10
		335	0.0504	0.0609			
1 ppm H ₂ S	260	167	0.0834	0.0966	62.8	53	1.18
		479	0.0311	0.0455			

* from reference [11]

Figure 1. Effect of 0.3-1 ppm H₂S on CO conversion over 100Fe/5.1Si/3K/2Cu. FTS conditions: 270 °C, 1.3 psig (CO+H₂), H₂/CO = 0.77, SV_{CO+H₂}=10 NL/g-cat/h and 260 °C, 1.3 MPa (CO+H₂), H₂/CO = 0.67, SV_{CO+H₂}=10 NL/g-cat/h.

Figure 2. Effect of 0.1-0.5 ppm H_2S on (a) CO conversion, and selectivities to (b) CH_4 , C_{5+} and CO_2 , (c) 1- C_4 olefin and 2- C_4 olefin, (d) total C_4 olefin and total C_4 paraffin over 100Fe/5.1Si/3K/2Cu. FTS conditions: 270 °C, 1.3 psig ($\text{CO}+\text{H}_2$), $\text{H}_2/\text{CO} = 0.77$, $\text{SV}_{\text{CO}+\text{H}_2}=10 \text{ NI/g-cat/h}$ and 260 °C, 1.3 MPa ($\text{CO}+\text{H}_2$), $\text{H}_2/\text{CO} = 0.67$, $\text{SV}_{\text{CO}+\text{H}_2}=10 \text{ NI/g-cat/h}$.

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Figure 6. Relationships between the amounts of surface iron lost and the amounts of sulfur introduced at different temperatures

Figure 7. Change in deactivation stoichiometry for the loss of surface Fe atoms per sulfur atom sorbed ($\text{H}_2\text{S} < 1.0$ ppm) with temperature.

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Figure 12. Relationships between the amounts of surface cobalt lost and the amounts of sulfur introduced at different temperatures