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Effect of H$_2$S in Syngas on the Fischer–Tropsch Synthesis Performance of a 0.5%Pt–25%Co–Al$_2$O$_3$ Catalyst

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Abstract The effect of 1.0 ppm H$_2$S in the syngas feed on initial activity and selectivity of a 0.5%Pt–25%Co/Al$_2$O$_3$ catalyst was studied by comparing the catalyst performance under H$_2$S and sulfur free conditions. The reaction tests were performed using a 1-L slurry phase reactor for 141–212 h under constant reaction conditions: 220 °C, 2.0 MPa, H$_2$/CO = 2.0 and 6.0 Nl/g-cat/h. In the H$_2$S poisoning test, an H$_2$S in N$_2$ gas mixture was added to the syngas feed (1.0 ppm) after running the Fischer–Tropsch synthesis (FTS) reaction for ca. 6.0 h; as such, the impact of H$_2$S on the initial deactivation of the cobalt catalyst (unsteady state) was successfully assessed. The used catalysts were characterized by XANES to investigate if Co–S surface species were formed during the deactivation. The initial deactivation under 1.0 ppm H$_2$S condition was significantly higher (by 2.0–2.4 times) than that under clean conditions. CH$_4$ selectivity increased substantially and C$_{5+}$ selectivity decreased greatly with time regardless of whether H$_2$S was added or not; however, the addition of H$_2$S accelerated the changes in the hydrocarbon selectivities, which were likely caused by the sharp deactivation of the catalyst in the presence of H$_2$S. After co-feeding the sulfur for 141 h, a comparison was made at similar conversions by adjusting space velocity; the sulfur pretreated cobalt catalysts favored heavier hydrocarbons (C$_{5+}$) formation and suppressed lower hydrocarbon formation. The addition of H$_2$S to the feed increased CO$_2$ selectivity and the secondary reaction of 1-olefins. The XANES results revealed that surface species involving Co–S bonding formed on the cobalt catalyst after exposure to H$_2$S during FTS. This was likely the primary reason for the abnormal selectivity trends observed during and after the deactivation of the catalyst by sulfur. This study points out a possible approach to increase the selectivity to heavy hydrocarbons by properly sulfiding the cobalt catalyst prior to the FTS reaction.

Graphical Abstract
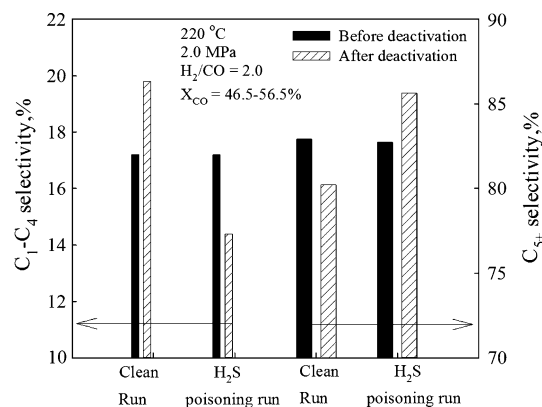
Keywords Fischer–Tropsch synthesis · Cobalt catalyst · XTL · Slurry phase reactor · H$_2$S · XANES

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1 Introduction

The effect of sulfur compounds, such as H$_2$S and COS, on cobalt or iron Fischer–Tropsch synthesis (FTS) catalyst, has been a very important topic in the processing of natural gas, coal and biomass to liquid fuels (XTL). Sulfur is one

of the impurities in the raw syngas derived from natural gas, coal or biomass that can severely deactivate catalysts, significantly reducing catalyst lifetime and liquid fuels productivity. Therefore, as a basis and guideline for purification of the raw syngas, defining how impurities in the raw syngas, like sulfur, impact FTS catalyst performance is an important challenge. Many sulfur poisoning studies on Co based catalysts in particular have been reported [1–8]. However, the results regarding the effect of sulfur on cobalt catalyst selectivity have not reached a consensus. We recently conducted sulfur poisoning studies over a Co/Al_2O_3 catalyst at 220–230 °C, 2.0 MPa using a 1-L continuously stirred tank reactor (CSTR) [6, 9]. A threshold limit (0.75 ppm) and the sulfur poisoning ability were determined, with one sulfur atom being reported to eliminate 31 Co atoms at 220 °C and 15 Co atoms at 230 °C [9]. Visconti et al. [7] studied the FTS performance of Co/Al_2O_3 catalysts when doping with 0–2000 ppm sulfur at 220 °C, 2.0 MPa and $H_2/CO = 2.0$ using a fixed-bed reactor. The sulfur decreased Co catalyst activity at all sulfur concentrations used and changes in catalyst selectivity depending on the sulfur level were reported; 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. Barrientos et al. [10] carried out a similar sulfur poisoning study using a $0.5\%Pt–12\%Co/Al_2O_3$ catalyst in a fixed-bed reactor at 210 °C and 2.0 MPa. 10–1000 ppmw of sulfur were doped onto the catalyst, which resulted in decreases in C_{5+} selectivity, increases in olefin hydrogenation and little change in CO_2 selectivity. In the study of Borg et al. [1], the effect of H_2S was examined by in situ cofeeding; several different sulfur levels (e.g., 2.5, 4.8 and 9.5 ppmv) were tested for about 200 h. It was reported that C_{5+} selectivity decreased at all sulfur levels, but these changes were ascribed to the CO conversion effect, and sulfur was reported to not affect the hydrocarbon selectivity. Thus, conclusions regarding the impact of sulfur on hydrocarbon selectivity are not in agreement. Moreover, the effect of deactivation or CO conversion on selectivity must also be considered, which complicates the analysis. Thus, it is important to continue to assess the effect of sulfur on cobalt catalyst selectivity; this may be achieved by judicious design of experiments, including by performing a clean run as well and examining the catalyst selectivity at similar conversion level before and after catalyst deactivation.

In this contribution, the effect of sulfur on the activity and selectivity of $0.5\%Pt–25\%Co/Al_2O_3$ catalyst were explored by introducing 1.0 ppm H_2S in situ after just a few hours of starting the FTS reaction, and also by performing a clean run in the CSTR. The changes in cobalt catalyst activity and selectivity with time under sulfur addition and sulfur free conditions were compared. After the severe deactivation of the catalyst under both conditions, the runs were brought back to close to the initial CO conversion level (i.e. 50 %) in order to understand how the selectivities change after the added sulfur modified the cobalt catalyst surface during deactivation. In this study, the selectivities to CH_4, $C_2–C_4$ and C_{5+} and olefins and paraffins ($C_2–C_4$) before, during and after the deactivation under clean and sulfur-containing conditions were carefully studied. The sulfur modified cobalt catalyst surface and decreased the selctivities of lower hydrocarbons (C_1–C_4) and increased the C_{5+} selectivity, an effect that was not completely addressed in previous sulfur poisoning studies. The characterization of the used cobalt catalysts by the XANES technique was performed; Co–S surface species on the used cobalt catalysts exposed to H_2S were detected, which was postulated to be a main reason for the selectivity changes for the sulfur deactivated cobalt catalyst.

2 Experimental

2.1 Catalyst Preparation

The $0.5\%Pt–25\%Co/Al_2O_3$ used in this study was prepared using a slurry phase impregnation method. The catalyst support used was Sasol Catalox-150 $\gamma-Al_2O_3$. Cobalt nitrate hexahydrate $(Co(NO_3)_2·6H_2O)$ (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 (tetraamine platinum (II) nitrate) was added to the Co/Al_2O_3 catalyst by incipient wetness impregnation. Only after the final step was the catalyst calcined under air flow at 350 °C for 4 h. The surface area of the $\gamma-Al_2O_3$ and $0.5\%Pt–25\%Co/Al_2O_3$ catalyst are 140 and 99 m^2/g, respectively [11].

2.2 XANES Characterization of Used Cobalt Catalysts

The electronic structure of sulfur and cobalt following catalyst poisoning was investigated by XANES near the S K-edge (fluorescence mode) and Co K-edge (transmission mode) at the Soft X-ray microcharacterization beamline (SXRMB) at the Canadian Light Source, Inc. The used catalyst sample, after H_2S poisoning in a continuously stirred tank reactor (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 software [12].

2.3 Fischer–Tropsch Synthesis Reaction

The 0.5%Pt–25%Co/Al_2O_3 catalyst ($\sim$15.0 g) was ground and sieved to 45–90 μm before loading into a fixed-bed reactor for 15 h of ex situ reduction at 623 K and atmospheric pressure using a gas mixture of H_2/He (60 NL/h) with a molar ratio of 1:3. The reduced catalyst was transferred to a 1-L continuously stirred tank reactor (CSTR) containing 315 g of melted Polywax 3000, under the protection of N_2 inert gas. The transferred catalyst was further reduced in situ at 503 K at atmospheric pressure using pure hydrogen (30 NL/h) for another 10 h before starting the FT reaction. The FTS conditions used in this study were 493 K, 2.0 MPa, H_2/CO = 2.0 and 6.0 NL/g-cat/h. To investigate the effect of H_2S on initial performance of the cobalt catalyst, 1.0 ppm H_2S was introduced after the FTS reaction was on-line for about 6 h. Before ending each catalytic testing run, CO conversion was brought back to $\sim$50 % CO conversion to determine whether the hydrocarbon selectivity trend changed for the sulfur treated cobalt catalyst. In total, three test runs lasting about 141–212 h were made for this study; one was a clean test run (no H_2S addition), and another was made with cofeeding H_2S; a third run was made to repeat the 2nd H_2S run in order to confirm the results obtained.

3 Results and Discussion

3.1 Effect of H_2S on the FTS Performance of a 0.5%Pt–25%Co/Al_2O_3 Catalyst

The effect of time on CO conversion, selectivities to CH_4 and C_{5+} (carbon atom basis), CO_2, 1-C_4 olefin, 2-C_4 olefin, total C_4 olefin, and total C_4 paraffin under H_2S and clean (sulfur free) conditions are shown in Fig. 1a–h. C_4 olefin or paraffin selectivity is defined as 100 × (rate of 1-C_4 or 2-C_4 alkenes or C_4 paraffins)/(rate of all C_4 hydrocarbons). Initial CO conversion of the cobalt catalyst decreased rapidly with time under the clean condition, as the deactivation rate in the first 52 h was significantly higher. From Fig. 1a, CO conversion decreased from 52.7 to 37 % in the first 52 h and then continuously decreased to 23.7 % at 212 h; these represent a deactivation rate (defined as the mean percentage of the activity decrease per hour, $Y = 100 \times (X_{CO,t0} - X_{CO,t})/X_{CO, t0}/(t - t_0))$ of 0.59 %/h in the first 52 h and 0.32 % between 52 and 212 h. In the sulfur test run, introducing 1.0 ppm H_2S at $\sim$6 h led to a much more severe deactivation of the cobalt catalyst. CO

conversion decreased sharply from 51 to 22 % in the first 45 h; in the next 96 h, CO conversion kept on dropping albeit at a slower rate, and it was only 8.6 % at 141 h. Thus, the addition of 1.0 ppm H_2S led to faster initial deactivation of the cobalt catalyst, and higher deactivation rates under the H_2S condition, 1.37 and 0.64 %/h in 0–45 and 45–141 h, respectively, were obtained compared to the results from the clean run. These results were reproduced in a repeated run with the addition of an identical concentration of H_2S (Fig. 1a). Thus, the initial deactivation of the cobalt catalyst under the H_2S condition originated from two aspects in addition to the effect of the solvent: one was cobalt sintering and/or cobalt oxidation, which is the same as in the clean run; another part was sulfur adsorption and deactivation. The results also indicate that the influence of on-line H_2S addition on the cobalt catalyst performance can initiate from the beginning of the reaction.

Figure 1b–d show the changes in CH_4, C_{5+} selectivity and CO_2 selectivity with time under sulfur-containing (1.0 ppm H_2S in the feed) and clean conditions. Regardless of whether or not H_2S was added, CH_4 selectivity increased significantly and C_{5+} selectivity decreased significantly with time; however, cofeeding of 1.0 ppm H_2S to the syngas feed accelerated the increases in CH_4 selectivity and the decreases in C_{5+} selectivity of the cobalt catalyst. In the clean run, a large increase in CH_4 selectivity i.e. from 7.5 to 11.5 %, and a large drop in C_{5+} selectivity, i.e. from 82.8 to 73.8 % in 212 h of testing were observed, which is a general selectivity trend with deactivation for a cobalt catalyst in the initial period of the run; however, in the presence of 1.0 ppm H_2S in the feed gas, CH_4 selectivity increased substantially to 25.2 % and C_{5+} selectivity decreased to 50.4 % in a shorter testing time, 141 h. The greater changes in the hydrocarbon selectivity with time in the H_2S test run could result primarily from the more severe deactivation under H_2S, since the effect of sulfur modifying the cobalt surface indeed played a positive effect on the C_{5+} formation and a negative effect on C_1–C_4 formation (to be further discussed). The trend of CO_2 selectivity with time changed greatly in the H_2S test run even though overall CO_2 selectivity on the cobalt catalyst was low, less than 1.6 %. In the first 50 h, CO_2 selectivities in the H_2S test run were slightly lower than those in the clean run, i.e. 1.6–0.8 versus 1.6–1.0 %; afterwards CO_2 selectivity in the H_2S run started to gradually increase and attained 1.6 % at 141 h, while it remained relatively constant in the clean test run (Fig. 1d). The result suggests that the introduced sulfur adsorbed on the cobalt catalyst surface modified cobalt surface structure, and consequently enhanced the extent of the WGS reaction. This speculation is consistent with the findings of XANES, which demonstrated new Co–S surface species in the H_2S poisoned cobalt catalyst (to be discussed).
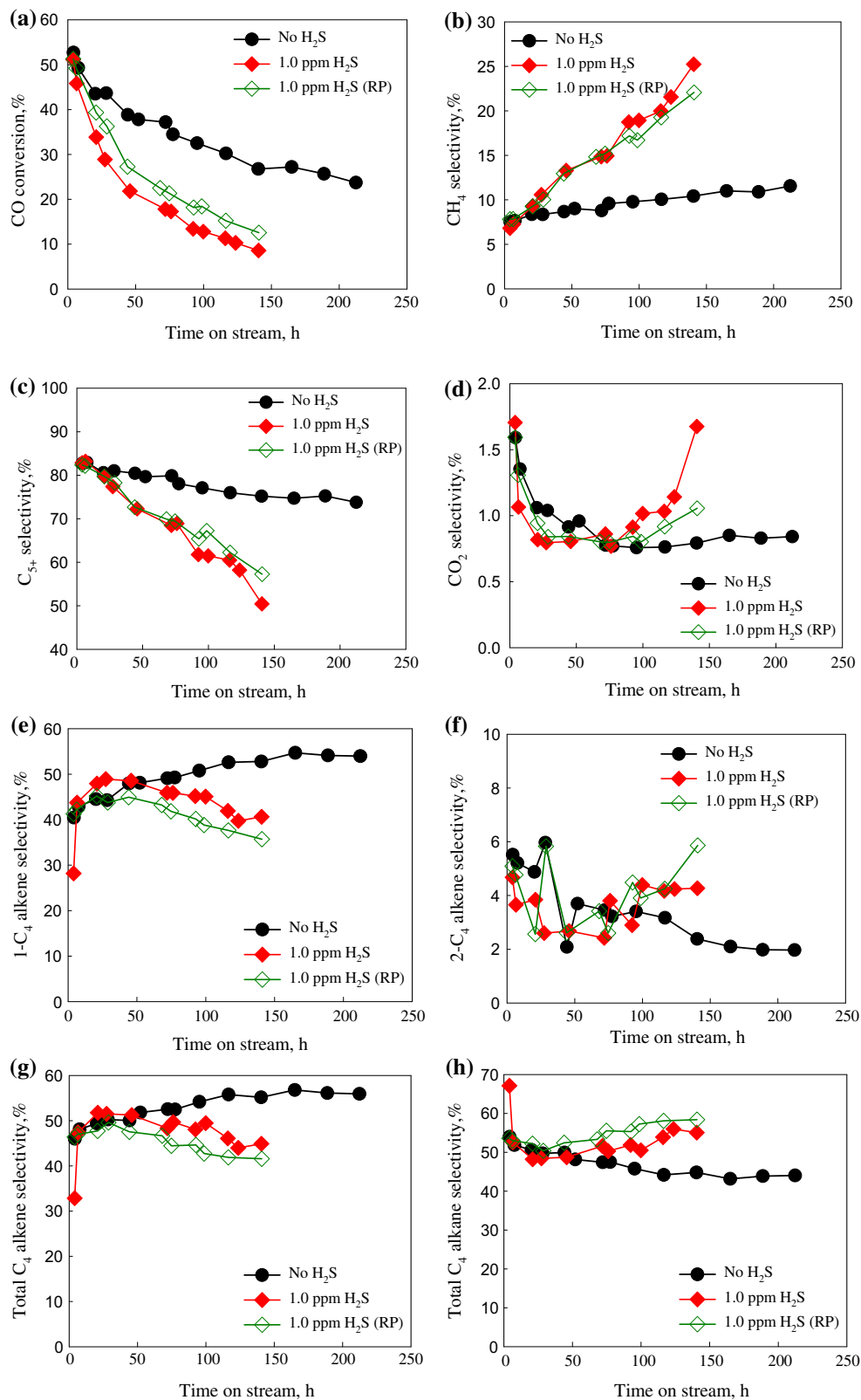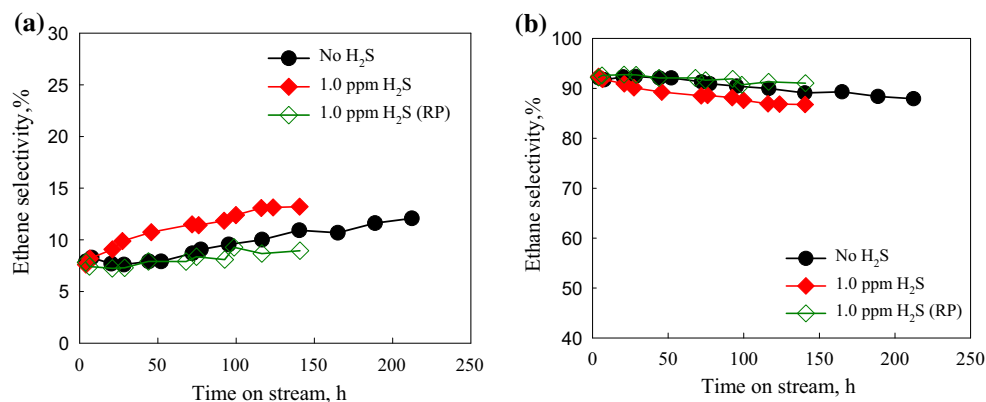
Fig. 1 Effect of 1.0 ppm H$_2$S and time on **a** CO conversion, and selectivities to **b** CH$_4$, **c** C$_{5+}$, **d** CO$_2$, **e** 1-C$_4$ olefin, **f** 2-C$_4$ olefin, **g** total C$_4$ olefin and **h** total C$_4$ paraffin over 0.5%Pt–25%Co/Al$_2$O$_3$. FTS conditions: 220 °C, 2.0 MPa, H$_2$/CO = 2.0, SV = 6.0 Nl/g-cat/h

The addition of 1.0 ppm H_2S to the syngas feed also changed olefin and paraffin selectivities. Figure 1e–h depict the changes in the selectivities to 1-C_4 olefin, 2-C_4 olefin, total-C_4 olefin and total-C_4 paraffin with time under 1.0 ppm H_2S and clean conditions. As expected, the selectivities to 1-C_4 olefin (40–54 %) and total-C_4 olefin (46–56 %) increased, and 2-C_4 olefin (5.5–2.0 %) and total-C_4 paraffin (54–44 %) decreased with deactivation in 141 h (Fig. 1e–h), since the secondary reactions (hydrogenation and isomerization) of 1-olefins to paraffins and 2-olefins weakened with deactivation on the FTS catalysts. In the presence of H_2S from ~6.0 h, the same selectivity trends as those under clean conditions were observed before 50 h; however, after that, opposite selectivity trends with time occurred, i.e. the selectivities to 1-C_4 olefin (48–39 %) and total-C_4 olefin (51–45 %) decreased, and those of 2-C_4 olefin (2.7–4.3 %) and total-C_4 paraffin (48–55 %) increased with deactivation between 50 and 141 h. These results may suggest that the changes in olefin and paraffin selectivities caused by sulfur were closely associated with the extent to which sulfur modified the cobalt surface to form Co–S species. It is speculated that the amount of Co–S surface species formed on the cobalt catalyst surface before 50 h was not high enough to result in pronounced impacts on the olefin and paraffin selectivities of the cobalt catalyst. As the reaction continued and additional H_2S was fed to the reactor, additional Co–S surface species were formed, consequently resulting in the unexpected and opposite selectivity trends. The repeated H_2S run reproduced the results and confirmed the roles of online feeding of H_2S on the selectivities of olefins and paraffins for the cobalt catalyst.

Note that the selectivity trends for the C_3 hydrocarbons (olefins and paraffin) are the same as the C_4 hydrocarbons as discussed above. For brevity, the results are not shown here. However, for the C_2 hydrocarbons, the addition of 1.0 ppm H_2S for 135 h did not alter the selectivity trends for ethane and ethene; namely, C_2 alkene selectivity kept on increasing (7.6–13 %) and C_2 alkane kept decreasing

(92.4–87 %) with time regardless of whether or not 1.0 ppm H_2S was added (Fig. 2). It could be that the ethene formed during FTS is much more active (~10 times) for the secondary reactions than other olefins (>C_3) [13]; therefore, the secondary reaction rate of ethene on the cobalt catalyst might decrease significantly with time or deactivation. In turn, small improvements in the secondary reaction of ethene resulting from the modification of the cobalt surface by sulfur (i.e. Co–S surface species, as observed by XANES) could not alter the selectivity trends of C_2 hydrocarbons.

Recently, the effect of H_2S on the selectivities to CO_2, 1-C_4 olefin, 2-C_4 olefin, total C_4 olefins, and total C_4 paraffins have been studied over an iron based catalyst [9]. The same findings, i.e. added H_2S increased CO_2 selectivity and hydrogenation of 1-C_4 olefins, were obtained. In another recent study by Barrientos et al. [10], the effect of sulfur on the activity and selectivity of 0.5%Pt–12%Co/γ-Al_2O_3 catalysts was investigated using a fixed-bed reactor at 210 °C, 2.0 MPa and H_2/CO = 2.1. In that case, 10, 100, 250, and 1000 ppmw sulfur were doped to the cobalt catalyst. Sulfur was reported to decrease C_{5+} selectivity and increase olefin hydrogenation; furthermore, it was reported that CO_2 selectivity was constant and not affected by the added sulfur. Thus, the selectivity results of olefins and paraffins except for CO_2 in the current study are consistent with that of Barrientos et al.

Our previous deactivation study on 0.27%Ru–25%Co/Al_2O_3 catalyst using XANES/EXAFS indicated that initial rapid deactivation of the cobalt catalyst (in the first 24 h) was due in part to cobalt sintering [14]. In another kinetic study using the same catalyst with a longer test period (~1200 h), the oxidation of cobalt to cobalt oxides and/or cobalt-aluminate were evident for the cobalt catalyst deactivation [15], in large part due to the excursions to high CO conversion where the partial pressure of H_2O was high. In both cases, the deactivation led to increased selectivities to CH_4 and 1-olefins, decreased selectivities to C_{5+} and 2-olefins, and nearly unchanged CO_2 selectivity, in line

Table 1 Comparison of the hydrocarbon selectivities of 0.5%Pt–25%Co/Al$_2$O$_3$ catalyst before and after the deactivation under clean and 1.0 ppm H$_2$S conditions (220 °C, 2.0 MPa, H$_2$/CO = 2.0)

TOS (h)	WHSV (h^{-1})	X$_{CO}$ (%)	Selectivity (carbon %)		CO$_2$ selectivity	
			CH$_4$	C$_2$–C$_4$	C$_{5+}$	(%)
Clean run						
7.6 h	6.0	51.01	7.59	9.56	82.85	1.47
236.3	2.4	56.52	8.30	11.47	80.23	1.92
1.0 ppm H$_2$S run						
6.3	6.0	49.20	7.55	9.72	82.73	1.07
178.3	1.3	46.47	8.49	5.89	85.61	1.23

with the current results. Therefore, according to the previous studies [14, 15], the deactivation under clean conditions in this study was probably due to cobalt sintering, although the oxidation of a fraction of tiny Co crystallites cannot be ruled out. In the presence of 1.0 ppm H$_2$S in the feed, much greater changes in the selectivities to CH$_4$ (increase) and C$_{5+}$ (decrease) with time were observed (Fig. 1b, c), suggesting that the added H$_2$S accelerated the marked hydrocarbon selectivity changes. However, the conclusion may be premature if the comparison of selectivities of different catalysts or the same cobalt catalyst under different process conditions was made at different conversion levels, for example in the above case during the deactivation before 141 h. Consequently, CO conversions after the severe deactivation in the H$_2$S run at 141 h and in the clean run at 212 h were brought back to about the initial value, i.e. ∼50 % by adjusting space velocity, such that the selectivity changes for the cobalt catalyst before and after the deactivation under clean and H$_2$S conditions could be accurately determined. Table 1 summarizes the hydrocarbon selectivities of 0.5%Pt–25%Co/Al$_2$O$_3$ in the 46.5–56.5 % CO conversion range.

The data in Table 1 obtained in the CO conversion range of 51–56.5 % in the clean run confirmed the results discussed in Fig. 1; that is, the deactivation of the cobalt catalyst for 212 h resulted in increases in the selectivities to CH$_4$ (7.6–8.3 %), C$_2$–C$_4$ (9.7–11.5 %) and CO$_2$ (1.5–1.9 %), and decreases in C$_{5+}$ selectivity (82.9–80.2 %). However, in the case of the H$_2$S poisoning condition, it clearly shows that the hydrocarbon distribution shifted to higher molecular weight hydrocarbons, with the C$_2$–C$_4$ selectivity decreasing significantly from 9.7 to 5.9 %, and C$_{5+}$ and CO$_2$ selectivities increasing from 82.7 to 85.6 and 1.07 to 1.23 %, respectively, at the CO conversion level range of 46.5–49 %. The results unambiguously suggest that H$_2$S treating of the cobalt catalyst for a certain time period suppressed the formation of lower molecular weight hydrocarbons (C$_2$–C$_4$) and promoted the formation of higher molecular weight hydrocarbons, as well as the water gas shift reaction. The XANES results of the used catalysts collected under clean and H$_2$S conditions indicate that the added sulfur modified the cobalt catalyst surface during FTS through the formation of Co–S surface species

(see Sect. 3.2), which were responsible for the observed hydrocarbon selectivity changes. It is interesting that the CH$_4$ selectivity after the severe deactivation under the clean and H$_2$S conditions at the CO conversion level of 46.5–56.5 % was similar, i.e. 8.30–8.49 % (Table 1). This would appear to be an indication of the formed Co–S surface species having no effect on CH$_4$ selectivity. However, taking into account that the CO conversion in the H$_2$S run (limited by the flow meter) was lower than that in the clean run (46.6 vs 56.5 %, Table 1), and normal catalyst aging processes (e.g., sintering, etc.) causing the deactivation in the clean run data was also a part of the deactivation path in the H$_2$S run, it is reasonable to expect to have lower CH$_4$ selectivity in the sulfur run than that in the clean run if CO conversion would be 56.5 %. It is therefore concluded that the Co–S surface species formed during the co-feeding of H$_2$S likely suppressed CH$_4$ formation in addition to suppressing the lower hydrocarbons, C$_2$–C$_4$. This result further supports the conclusion that the greater changes in CH$_4$ and C$_{5+}$ selectivities during cofeeding of 1.0 ppm H$_2$S (Fig. 1a) were mainly due to the CO conversion effect.

3.2 XANES Spectroscopy Results

The XANES spectra of the catalyst after running under clean (two separate runs) or after H$_2$S poisoning at the Co K-edge are shown in Fig. 3 (left). Comparing with the reference compounds, the catalyst after running under clean conditions displays spectra consistent with primarily a mixture of Co metal and some residual unreduced CoO. The used H$_2$S poisoned catalyst has a lower white line due to the fact that it was run for a longer duration of time, consistent with some net reduction. However, an additional shoulder appears in the spectrum of the H$_2$S poisoned catalyst. Co K-edge XANES difference spectra are shown in Fig. 4. There are clearly two separate peaks, one which is consistent with residual CoO (as observed in the cases of the clean run catalysts), and an additional shoulder at lower energy. A comparison with spectra for CoS and Co$_2$S indicates that this shoulder matches well with the formation of, in part, a Co–S compound.

Fig. 3 XANES spectra of the H₂S poisoned used Co catalyst in comparison with the spectra of reference compounds at the K edges of (left) Co and (right) S
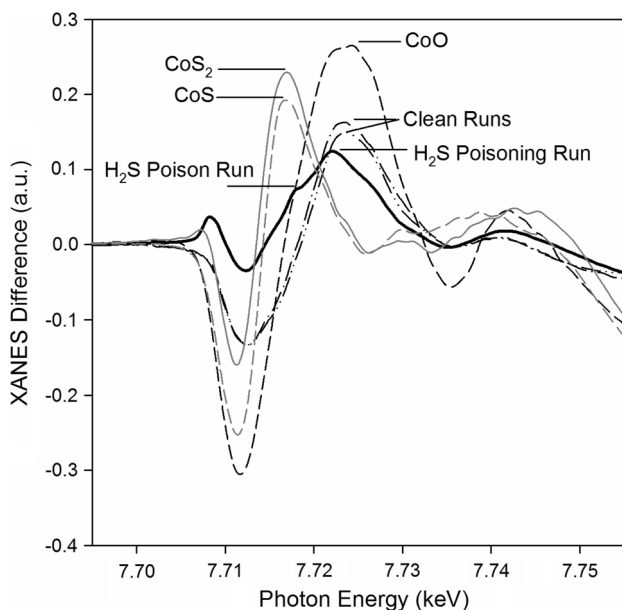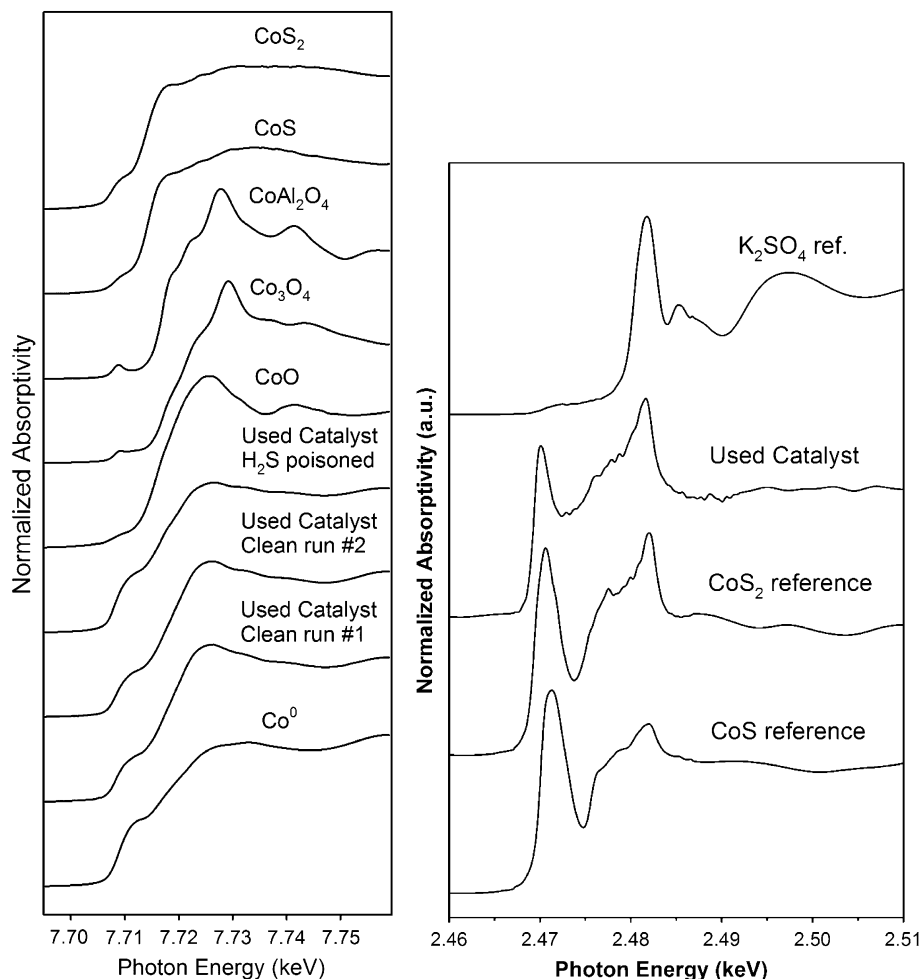

Fig. 4 XANES difference spectra at the Co K-edge using Co^0 foil as the references of the H₂S poisoned used Co catalyst in comparison with the spectra of reference compounds

Analysis at the S K-edge, as shown in Fig. 3 (right), reveals unambiguously that S is indeed present on the catalyst following H₂S poisoning. Two pronounced features in XANES were detected, including a significant low energy peak at ~ 2.47 keV, associated with a surface cobalt sulfide species, and a higher energy peak at ~ 2.482 keV. The latter peak is associated with a surface sulfate. This may be located on the residual CoO in the catalyst. Even the reference compounds had a low intensity peak associated with some residual sulfate.

Note that the above discussion regarding the effect of sulfur on cobalt catalyst activity and selectivity was made with a 0.5%Pt promoted 25%Co/Al₂O₃ catalyst. Thus, whether the Pt promoter played a role on the sulfur effect and impacted the above conclusion is worthy of discussion. The primary role of Pt is to facilitate reduction of cobalt oxides significantly interacting with the support, thereby substantially increasing the Co metal site density relative to an unpromoted catalyst [16–20]. Therefore, if sulfur poisoning of Pt sites is responsible for maintaining Co in a metallic state, then one would expect an increase in CoO

content. However, this is not the case. The catalyst, in fact, continued to reduce slightly in agreement with the complex aging mechanism involving net reduction/sintering proposed in the literature based on extensive XANES investigations by CAER and Sasol researchers [21, 22]. Thus, once Pt facilitates reduction of Co oxide species interacting with the support, those metallic cobalt particles remain reduced during sulfur-poisoning and any blocking of Pt by S does not affect the oxidation state of those Co particles. From our prior EXAFS investigations, Pt is found to be in intimate contact with Co at the atomic level [23]. We cannot rule out that sulfur does bind with Pt atoms. Regarding selectivity, Pt addition to Co/alumina catalysts has been found to slightly increase light gas selectivity and decrease $C_{5}+$ relative to an undoped Co/alumina catalyst, and this may be due to enhanced H_2 dissociation and spillover during FTS (i.e., from slightly enhanced chain termination) [16]. Thus, if S blocking Pt sites is responsible for enhancing H_2 dissociation and spillover, this factor, albeit minor, could contribute to the decreased light gas selectivity observed after sulfur poisoning. However, the changes in hydrocarbon selectivity observed after sulfur poisoning are primarily due to modification of the cobalt surface by sulfur.

4 Conclusions

The effect of co-feeding 1.0 ppm H_2S on the initial activity, selectivity and Co phases of 0.5%Pt–25%Co/ Al_2O_3 catalyst was studied by conducting the FTS reaction in the CSTR and performing XANES characterization of used cobalt catalysts. The FTS reaction under H_2S poisoning and clean conditions (no H_2S) was performed under constant reaction conditions, 220 °C, 2.0 MPa, H_2/ CO = 2.0 and 6.0 NL/g-cat/h, for 141–221 h.

The initial deactivation in the H_2S test run was significantly higher (2.0–2.37 times) than that of the clean run. Under the H_2S condition the initial deactivation originated from two aspects, sulfur adsorption/site blocking, and normal aging (e.g., cobalt sintering, etc.) that was also the main cause of the deactivation under clean conditions. During the deactivation, regardless of the presence or absence of sulfur, CH_4 selectivity increased and C_{5+} selectivity decreased significantly, which was ascribed to the CO conversion effect. After the severe deactivation, the hydrocarbon selectivities were compared at similar CO conversion levels (46.5–56.5 %). It was found that the sulfur treated cobalt catalyst indeed favored heavier hydrocarbon (C_{5+}) formation and suppressed lower molecular weight hydrocarbon formation. This was

primarily due to the added H_2S modifying the cobalt catalyst surface (forming Co–S bonds) that might hinder chain termination. The results could indicate an approach to increase the selectivity to heavy hydrocarbons, C_{5+}, i.e. by properly sulfiding the cobalt catalyst prior to starting the FTS reaction.

The Co–S surface species formed during cofeeding H_2S were proposed to be responsible for the increased secondary reactions (hydrogenation and isomerization) of 1-olefins and the increased extent of WGS reaction. Unlike C_3 and C_4 hydrocarbons, the selectivity trends with time for ethene and ethane were not changed by the added sulfur, which could be due to ethene being much more active than other olefins. That is, the decrease in the hydrogenation of ethene was very sensitive to the steep deactivation, such that the added sulfur did not significantly affect it.

The used catalysts after tests under the 1.0 ppm H_2S or sulfur free conditions were characterized by XANES. The results suggest that the added sulfur modified the cobalt surface to some extent, and surface compounds involving Co–S bonds were detected on the used cobalt catalysts after they were poisoned by the H_2S for 135 h. The new Co–S species formed along with the CO conversion played a dominant role on the observed changes in product selectivities.

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