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Iron Removal from High-Temperature Fischer–Tropsch-Derived Distillate through Thermal Treatment

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S Supporting Information

ABSTRACT: Hydrotreating units at the Sasol high-temperature Fischer–Tropsch plant in Secunda, South Africa, experience a number of unplanned shutdowns because of sudden increases in pressure over the reactor beds. This is caused by a solid crust that builds up at the top of the catalyst bed. The crust constituents were studied using inductively coupled plasma (ICP), and it was found that the major constituents of the crust are iron (48 mass %) and sulfur (28 mass %), in the form of iron sulfide (Troilite), as confirmed by X-ray diffraction (XRD) spectroscopic techniques. FeS is believed to originate from dissolved iron carboxylates present in the feed streams. A range of aliphatic iron carboxylates (C_5 – C_{11}) expected to be present in the distillate hydrotreater feed were subsequently synthesized and characterized using infrared (IR) spectroscopy. The thermal behavior of these carboxylates was studied using high-pressure differential scanning calorimetry (HP-DSC); decomposition temperatures established ranged from 299 to 282 °C from C_5 to C_{11} . It has been shown experimentally that iron carboxylates dissolved in feed streams may be thermally decomposed *in situ* and removed as iron sulfide or iron oxide in the presence or absence of H_2S , respectively. High-pressure hydrogen or nitrogen may not be necessary during thermal decomposition of the iron carboxylates. However, hydrogen gas may be necessary to prevent coking but has no significant role in iron carboxylate decomposition. Therefore, iron carboxylates may still be decomposed and removed effectively from the feed streams using an upstream guard bed even at pressures lower than those used in the hydrotreating reactor.

1. INTRODUCTION

Hydrotreating technology is one of the widely used refinery processes in the world. Since the 1950s, there are more than 500 licensed units worldwide.¹ Hydrotreating is designed to improve the quality of residue, distillate, and naphtha streams by removing heteroatoms, such as nitrogen, oxygen, and sulfur by hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), and hydrosulfurization (HDS), respectively.² A number of refineries and chemical process plants suffer to some degree from catalyst bed plugging,³ which results in an increased pressure drop over the reactor and/or accelerated catalyst deactivation. Catalyst fouling leads to unnecessary and expensive shutdowns, catalyst replacements, or a skim of catalyst material, even though it may still be active. This has a negative impact on productivity and profitability.

The foulants that cause plugging can arise from a number of sources. The majority of foulants are contained in the feed and might have been generated from either corrosion of the upstream equipment during piping and storage or leaching and attrition of the catalysts used upstream. Deposition occurs in the hydrotreater catalyst bed, which reduces the void fraction in the bed. As a result, catalyst activity is decreased as the fouling narrows the pore mouth and/or through encapsulation of the catalyst surface.³ Foulants are categorized into three different groups, namely, particulates, reactive molecules in the feed, and inorganic poisons.⁴

In crude oil refineries, the feed may contain a wide combination of solid particles, including clays, coke, and corrosion products, such as iron oxides and iron salts. These particles deposit in catalyst beds and cause premature shutdowns.² Clay particles have been seen in units processing

Athabasca bitumen.^{5a} Fouling has also been noted on furnaces used during processing of Athabasca oil sands bitumen, and such feed contains a high concentration (300–450 ppm) of iron from the inorganic matrix.^{5b} Iron oxides and iron salts, such as sulfates, chlorides, and carbonates, are carried through to the hydrotreater during crude oil processing. These are then converted to iron sulfide in the hydrogen-sulfide-rich hydrotreating environment.⁶ It has been noted that, even at low H_2S partial pressure, iron oxide is easily converted to iron sulfide.²

A number of research groups have directed their attention toward the understanding of hydrotreating reactor bed plugging because of fine particles, and a number of fouling mechanisms and simulation models have been reported.^{7–10} It has been noted that filtration of the feed prior to the hydrotreater can effectively remove the $>20\ \mu\text{m}$ particles but not all of the $<20\ \mu\text{m}$ fines.^{7,10} Gray et al. reported that particles in the colloidal range ($<1\ \mu\text{m}$) tend to deposit evenly along the catalyst bed.¹¹ Wang et al. reported that, for the $<20\ \mu\text{m}$ to deposit and narrow the flow channels in packed bed reactors, they must accumulate by multilayer deposition.¹⁰ For retention of fines to occur, the attractive forces between particles must be strong enough to withstand removal by high forces from the feed flows.¹⁰ Despite the low concentration of the fines, the cumulative effect of thousands of liters of feed per day converts the catalyst bed into a gigantic filter, collecting hundreds of kilograms of fines.⁷ This leads to high pressure drop and

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premature shutdowns, and the still chemically active catalyst has to be replaced.

However, hydrotreaters processing distillates and naphtha derived from the high-temperature Fischer–Tropsch (HTFT) facility of Sasol in Secunda, South Africa, experience fouling originating from the decomposition of dissolved organic iron complexes under H_2S -rich hydrotreating conditions. Iron carboxylates of varying chain lengths are believed to be formed during carboxylic acid corrosion during piping and storage of the feedstock. The issue of carboxylic acid corrosion and the formation of iron carboxylates is not unknown to the crude oil refiners.¹² The type of organic acids found in crude oils are referred to as naphthenic acids, because they are a complex mixture of several cyclopentyl and cyclohexyl carboxylic acids with varying molecular weights from 120 to 700 amu. The U.S. Southern Gulf Coast Refinery processing a blend of Venezuelan crude oils experienced naphthenic acid corrosion in the vacuum heater transfer lines, the heavy vacuum gas oil (HVGO) section of the vacuum tower, and the piping.¹³ This refinery mitigated the corrosion effects by the use of corrosion inhibitors, which lay a protective layer on the metal surfaces to inhibit corrosion.¹³ It has been reported that naphthenic acids cause corrosion in units operating above 230 °C. Such corrosion has been seen in heater tube outlets, pumps, column flash zone, and transfer lines.¹⁴ Xinqiang et al. have proven experimentally that A3 carbon steel has little resistance to naphthenic acid corrosion, especially in sections where the temperature, total acid number (TAN), and flow velocity are higher.^{15a} A number of oil-processing industries have developed technologies to mitigate fouling, such as iron adsorption technologies,^{15b} magnetic separation,^{15c} or macroporous traps,^{15d} to name a few. Some of these technologies require extensive capital investment and rigorous operating conditions, and these seem to work better in the removal of the particulate matter. Liu et al. reported that polyamine- and organophosphate-type agents are better deferrization agents for crude oils containing solid and dissolved iron.^{15e} Nevertheless, soluble iron removal is still not well-understood.

The hydrotreating units of the HTFT plant of Sasol are designed to hydrotreat a combined stream of vacuum gas oils (VGO, both light and heavy vacuum gas oils), coker gas oil (CGO), and the bottom fraction of stabilized light oil (SLO) to produce naphtha and light distillate. The feed stream is highly olefinic, predominantly α -olefins, and has a high oxygenate content, which includes alcohols, aldehydes, ketones, and carboxylic acids.^{16,17} These organic acids are believed to cause corrosion and plugging. Hydrotreating is normally achieved through the use of commercial catalysts, such as nickel–molybdenum (Ni/Mo), nickel–tungsten (Ni/W), nickel–cobalt–molybdenum (Ni/Co/Mo), or cobalt–molybdenum (Co/Mo) combinations.¹⁸ These catalysts require activation by the addition of a small amount of sulfur, and this is usually performed by the addition of a sulfiding agent, such as dimethyl disulfide (DMDS), to the sulfur-free feed.¹⁷ On the other hand, hydrotreating with unsulfided catalysts, such as Ni on Al_2O_3 , is disadvantageous, because the acids contained in the HTFT-derived feed tend to leach the metal from the catalyst.¹⁸

Pressure drop through fouling leading to a solid crust that builds up at the top of the catalyst bed has become a serious concern. The fouling mechanism is not completely understood, and there are presently no viable engineering solutions available. Catalyst skims are performed frequently to mitigate pressure drops. Because there is no sufficient literature

precedence on how to alleviate reactor bed plugging caused by dissolved iron carboxylates, determination of the foulant constituent and iron carboxylate decomposition temperatures may contribute toward establishing a technology solution to this type of bed plugging.

2. EXPERIMENTAL SECTION

2.1. Materials. Crusts (foulant) obtained from the commercial hydrotreating reactor were the basis for the foulant identification study. Chemicals for the synthesis of iron carboxylates were obtained from the listed suppliers and were used without further purification: acetic acid and iron powder (Riedel-de Haën); valeric acid, hexanoic acid, nonanoic acid, decanoic acid, and undecanoic acid (Aldrich); dodecanoic acid (Sigma); and octanoic acid (Sigma Life Science).

For the thermal treatment study, DMDS was obtained from Sigma and used without further purification. The same commercial catalysts used as top catalysts in a graded system of beds in hydrotreating reactors were used in the experiments. The C_9 – C_{11} paraffin mixture used as a solvent was obtained from Sasol. The model feed was a combination of the C_5 – C_{11} freshly prepared iron carboxylates dissolved in a C_9 – C_{11} paraffin mixture. The distillate hydrotreater feed streams were provided by the commercial HTFT plant.

2.2. Analysis. Crust, spent catalyst, feed, and product samples were analyzed on a Perkin-Elmer Optima 4300 DV inductively coupled plasma (ICP) spectrometer. The progress of iron carboxylate formation and the final products was analyzed using an ABB Bomem Arid Zone Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1} , equipped with a PikeMiracle high-pressure clamp system. Thermal analyses were performed on a Mettler Toledo DSC 827^e high-pressure differential scanning calorimeter (HP-DSC) with a FR55 sensor. Elemental analyses were performed on Leco TruSpec-CHN, Leco TruSpec-S, and ICP spectrometers. Thermogravimetric analysis (TGA) was performed using a Mettler TGA/SDTA 851^e thermogravimetric instrument, under a nitrogen atmosphere. ^{57}Fe Mössbauer studies were performed using an in-house constant acceleration spectrometer in a triangular mode with a 50 mCi $^{57}\text{Co}/\text{Rh}$ source. Analysis of demetallized feed samples was verified using the Agilent 7500 series ICP spectrometer.

2.3. Foulant Identification. The samples were first calcined at 500 °C for 2 h in a furnace to burn off the coke. Elemental and CHNS analyses were conducted to determine the amounts of carbon, hydrogen, nitrogen, and sulfur on both uncalcined and calcined samples. Quantitative and qualitative X-ray diffraction (XRD) analyses were performed on the samples to determine the phases of major constituents of the crust.

2.4. Typical Synthetic Approach. A modified synthetic approach initially patented by Welsh was employed in this study to prepare iron carboxylates of interest as follows:¹⁹

Iron powder was weighed into an oven-dried, nitrogen-purged 250 mL two-necked round-bottom flask, equipped with a reflux condenser and a magnetic stirrer bar, where after 50 mL of toluene was added as the reaction solvent. A slight excess amount of the appropriate acid was added slowly to this mixture through the dropping funnel. Solid acids were predissolved in a separate flask and added slowly to the flask containing the slurry of iron and toluene. The flask contents were purged with nitrogen for 5 min under continuous stirring and allowed to heat from ambient to 140 °C in an oil bath. The resulting mixture was maintained at this temperature under continuous stirring until reaction completion. During reflux, the reaction mixture turned dark brown in color as the iron powder was gradually consumed and converted to the desired iron carboxylate.

Reaction completion times varied from 2 days to 2 weeks depending upon the carbon chain length of the carboxylic acids. For longer reaction times, solvent evaporation was compensated by subsequent additions of toluene, if required. FTIR spectroscopy was used to monitor the progress of the iron carboxylate formation. Upon reaction completion, the solvent was removed using a Büchi rotavapor (under continuous vacuum, with the oil bath temperature set to 60 °C). The desired iron carboxylates were obtained as dark brown clay-like

materials. Because of the hygroscopic nature of the iron carboxylates, the freshly prepared samples were purged and stored under nitrogen in a cold storage facility.

2.5. Feed Demetallization through Thermal Treatment. A stainless-steel batch autoclave reactor system was loaded with a mixture of the feed system under investigation, the commercial catalysts, and DMDS (1 wt %). The reactor was then flushed several times with nitrogen and leak-tested at 60 bar nitrogen, at which nitrogen was then vented and the reactor was pressurized to 35 bar with hydrogen. The autoclave was subsequently heated to the reaction temperature (300 °C), while the internal pressure increased upon heating to ~50 bar. The contents of the reactor were stirred continuously at 200 rpm. It took approximately 20 min for the reactor to reach the set temperature. The first sample was taken under pressure as soon as the set temperature was reached. Subsequent samples were then taken at 20 min intervals. DMDS was not used for unsulfided experiments; nitrogen or hydrogen was used instead. All samples were filtered through 6 μ m filter paper prior to analysis.

3. RESULTS AND DISCUSSION

3.1. Foulant Identification. The crust sample from the commercial hydrotreater had a black appearance, which upon calcination turned reddish brown in color, which is indicative of the presence of an iron-containing species. ICP and CHNS analyses of the uncalcined crust showed that the major elements are iron and sulfur (entries 4 and 17 in Table 1).

Table 1. ICP and CHNS Analyses of the Uncalcined Crust Sample

entry	elements (by ICP and CHNS)	amount (mass %)
1	Al	<0.010
2	Ca	<0.010
3	Cu	<0.010
4	Fe	48
5	Mg	<0.010
6	Mn	<0.010
7	Mo	0.040
8	Na	0.11
9	Ni	0.93
10	Si	0.15
11	Ti	<0.010
12	V	<0.010
13	W	<0.010
14	C	0.80
15	H	0.20
16	N	0.00
17	S	23
18	moisture	0.070
19	ash	86

Other elements, such as vanadium and titanium, which are potential poisons to the catalyst, were found in concentrations of less than 0.01 mass %. The carbon content was on the order of 0.8 mass % (entry 14 in Table 1). Infrared analysis showed no evidence of hydrocarbon stretching frequencies. The nickel content (ca. 0.93 mass %) was slightly higher than that of other transition-metal elements, excluding iron (entry 9 in Table 1).

As shown in Table 1, iron and sulfur are the major constituents of the crust, but these results do not disclose the structure of the iron and sulfur compounds. A possible compound that comes to mind is pyrite FeS₂ (fool's gold) that is found in coal beds and fossils containing a combination of iron and sulfur. XRD patterns (Figure 1) verified that the crust is composed of iron, sulfur, and nickel in the form of

hexagonal crystalline troilite (FeS) as a major compound, metallic iron (cubic crystals), and low traces of pentlandite Fe₄Ni₅S₈ (cubic crystals). Calcination of the crust in a furnace resulted in the complete oxidation of the iron species to iron oxides, such as maghemite (γ -Fe₂O₃) and hematite (α -Fe₂O₃).

The formation of FeS could be attributed to the decomposition of iron carboxylates, in the presence of H₂S originating from the sulfiding agent DMDS (Scheme 1). The decomposition of transition-metal carboxylates has been reported to occur via the formation of free metal and carboxylic acid radicals.²⁰ In addition, the suggested formation of FeS is a thermally driven process that occurs as soon as the feed containing dissolved Fe carboxylates enters the top of the hydrotreater. The temperatures at that point are high enough to drive the formation of FeS precipitate. The function of the catalyst in this case is to generate H₂S. In the absence of H₂S, decomposition of metal carboxylates is known to yield metal oxides and other byproducts, such as CO, CO₂, H₂, water, ketones, esters, and alkanes of different chain lengths. The formation of iron oxide nanocrystals has been reported to occur during decomposition of Fe(OAc)₂²¹ and iron decanoate at temperatures ranging from 140 to 245 °C and pressures of about 0.4–1.6 MPa.²² Alternatively, if unsulfided catalysts, such as reduced Ni on Al₂O₃, were used, the Fe carboxylates would decompose to magnetite Fe₃O₄ or hematite Fe₂O₃ nanocrystals, which would also result in crust formation and, subsequently, pressure drops. Nevertheless, unsulfided Ni catalysts are not applied for hydrotreating of HTFT distillates because the acids in the feed tend to leach the metal from the catalyst.²³

3.2. Thermal Behavior of Prepared Iron Carboxylates.

Calorigrams acquired from decomposition of synthesized iron carboxylates displayed a number of remarkable transitions as the temperature is increased from ambient to 500 °C. Of particular interest were the most prominent transitions above 250 °C, characterized by sharp to broad endotherms attributed to decomposition of the iron carboxylates under investigation (Figure 2).

Davis and Schultz reported that short-chain iron carboxylates derived from acetic and propionic acids are more stable up to 400–500 °C.²⁴ As expected, in our study, the C₅ iron carboxylates started decomposing at 298 °C. XRD analysis of the decomposition products showed that iron carboxylates decomposed to a mixture of iron oxides, hematite (α -Fe₂O₃) and magnetite (Fe₃O₄). It was of particular interest to note that, as the carboxylate chain length increases, the decomposition temperatures drop by approximately 2–4 °C per carbon number, down to ~280 °C from C₅ to C₁₁. Differential scanning calorimetry (DSC) analysis has demonstrated that the C₅–C₈ iron carboxylates, which are believed to be major contributors to the hydrotreater fouling, decompose at a temperature range of 300–290 °C. On the other hand, C₉–C₁₁ carboxylates decompose at a range of 285–280 °C (Figure 3). However, their parent acids have been reported to exist in a very low concentration in the hydrotreater feed stream.

A number of noteworthy facts that could be influential in the efforts to mitigate bed plugging have been drawn from the above findings; that is, decomposition of iron carboxylates seems to be a thermally driven process. It is speculated that iron carboxylates of varying chain lengths are converted to iron sulfide (FeS) at hydrogen-sulfide-rich hydrotreating conditions (Scheme 1). However, the exact structure of the iron complexes formed during acid corrosion has not been fully elucidated, and it is uncertain whether Fe²⁺ or Fe³⁺ carboxylate complexes are

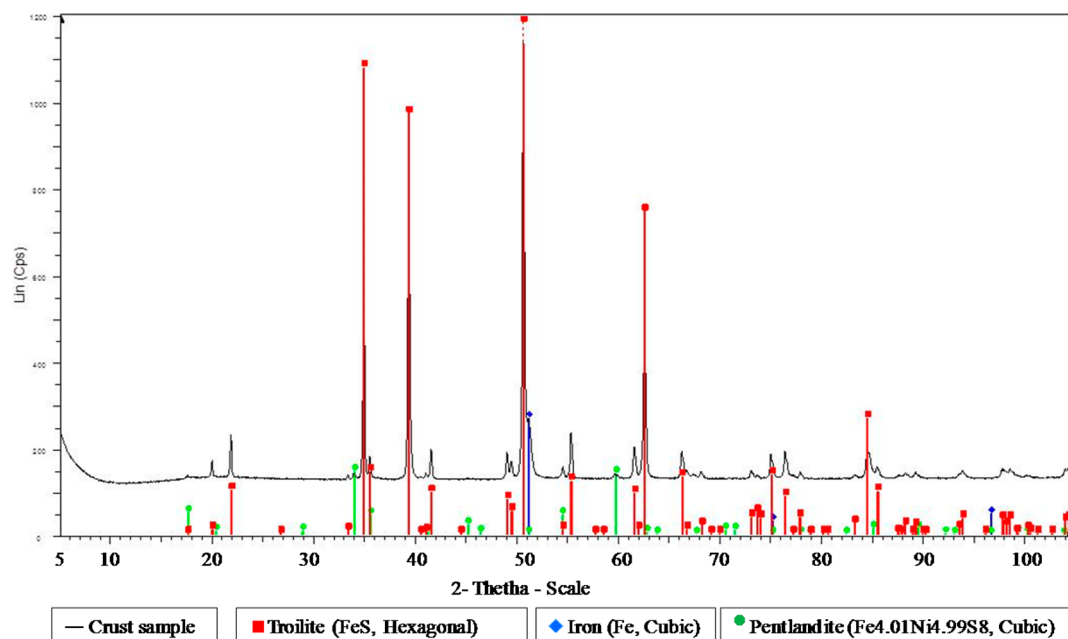
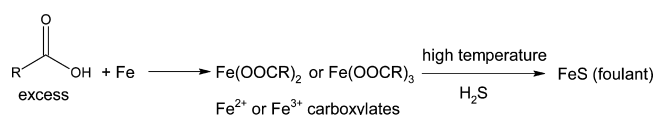


Figure 1. XRD patterns of the uncalcined foulant.

Scheme 1. Formation of Fe^{2+} or Fe^{3+} Carboxylates and Conversion to FeS at Hydrotreating Conditions



formed during carboxylic acid corrosion. The above decomposition temperature range is based on prepared Fe(III) carboxylates, as corroborated by Mössbauer spectroscopy (Figure 4), which consisted of two absorptions, with isomer shift (δ) values ranging from 0.42 to 0.44 mm/s and the quadrupole splitting (ΔE_Q) values ranged from 0.55 to 0.62

mm/s for prepared C_5 , C_7 , and C_9 iron carboxylates. These results are in agreement with those by Dziobkowski et al. for the Fe(III) acetate, malonate, and succinate complexes.²⁵

3.3. Demetallization of the Feed through Thermal Treatment. Thermal treatment as a means to test demetallization of feed was initiated using the model feed containing C_5 – C_{11} iron carboxylates in a C_9 – C_{11} paraffin mixture. The model feed was designed to have a decreasing distribution of iron carboxylates as the carbon chain length increases, to simulate the acid distribution in the real feed used in the synfuel hydrotreater.

The demetallization studies were conducted in the presence of DMDS to generate H_2S under 50 bar of hydrogen pressure

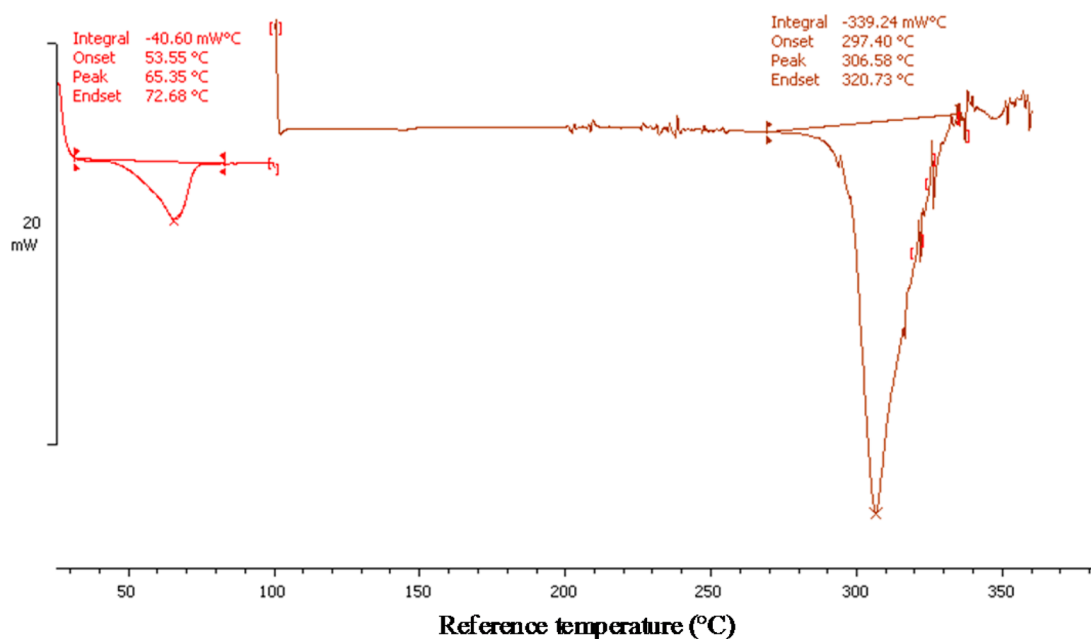


Figure 2. DSC calorigram for decomposition of iron hexanoate.

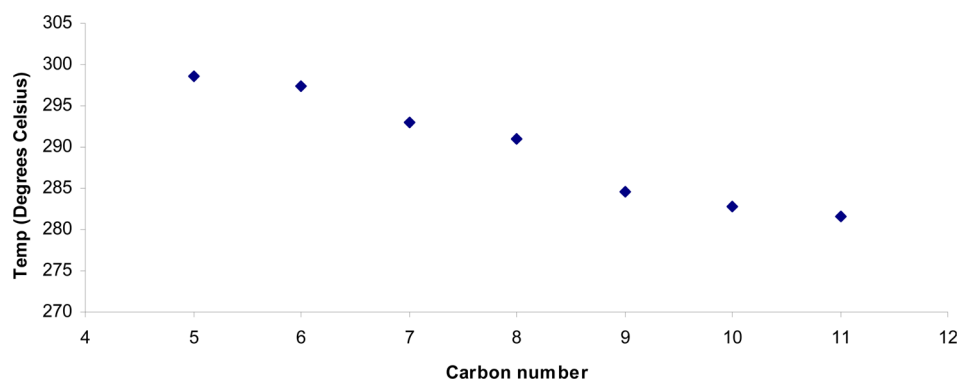


Figure 3. Decomposition temperatures of synthesized C_5 – C_{11} iron carboxylates.

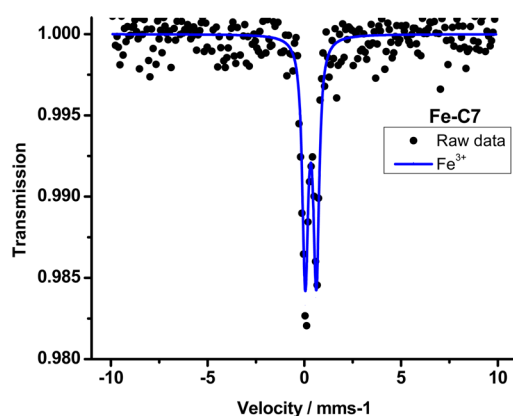


Figure 4. Typical Mössbauer spectra acquired from a C_7 iron carboxylate at 298 K.

at 300 °C. Duplicate experiments were performed in the absence of DMDS under an inert atmosphere of high-pressure nitrogen. The reaction temperature was adopted from the thermal decomposition study discussed above. As expected, the ICP analysis of thermally treated and filtered samples taken in 20 min intervals showed that dissolved iron carboxylates may be removed effectively from the feed material as iron oxides in the absence of H_2S or iron sulfide in the presence of H_2S . It was of special interest to note that, in the presence of H_2S , the iron concentration in the model feed drops by approximately 25-fold in 40 min, as compared to a 1.5-fold drop in the absence of H_2S (Figure 5).

An apparent advantage in the presence of H_2S was that the samples became clearer over the time period. This may be attributed to the fact that the FeS formed *in situ* during decomposition was noted to adhere more onto the catalyst

surface, reactor wall, impeller, and dip tube. While on the other hand, in the absence of H_2S , samples were darker. It was also noted that some of the iron oxide particles formed were suspended in the feed and, therefore, carried out through the dip tube. Even after settling for 24 h followed by subsequent filtration, these samples were still darker, indicating the high iron content, as evident in the ICP analysis above (Figure 5).

The finely divided iron oxide particles observed in our experiments may be related to the findings by Kwon et al., who reported that thermal decomposition of an iron–oleate complex led to the formation of iron oxide nanoparticles.²⁰ Konishi et al. found hematite (α - Fe_2O_3) and magnetite (Fe_3O_4) through thermal decomposition of an iron carboxylate complex derived from versatic 10 solution.²² At high temperature and pressure, crystalline particles of magnetite with sizes of ca. 0.1 μm were formed.²² Judging from our experimental findings and the above literature citations, it must be noted that, if a guard bed is used to decompose organic iron compounds to the oxides, the formed oxides may not deposit well on the surface of the guard bed material and, therefore, be carried over by the feed to the hydrotreater. Moreover, the particle size is in the colloidal range and may pose difficulties in filtration as previously reported.^{7,10}

Duplicate experiments using commercial feed used in the synfuel hydrotreating units were conducted, with the intention to test the viability of thermal treatment as a solution to iron-based foulant removal. The thermal treatment method was highly effective, reducing the iron concentration from approximately 10.1 mg/kg to a low of 0.92 mg/kg in the absence of H_2S in 2 h (Figure 6). It was of importance to note that the role of H_2S becomes negligible after ~ 100 min and all curves seem to merge toward approximately the same iron content (Figure 6). On the other hand, in the model feed used

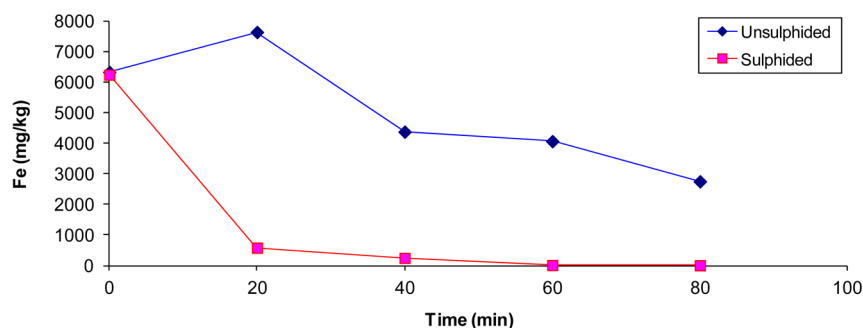


Figure 5. Iron content of thermally treated and filtered model feed samples.

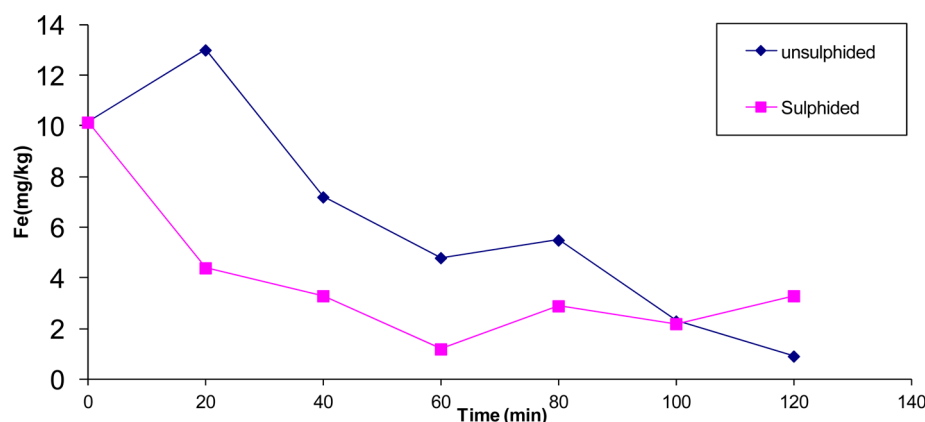


Figure 6. Analysis of the iron content in thermally treated and filtered hydrotreater feed material.

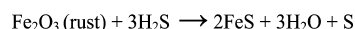
previously, with a high iron content, the role of H_2S was highly pronounced.

These observations clearly show that the iron-containing hydrotreater feed material may be demetallized effectively through thermal decomposition in an *ex situ* guard bed system with or without H_2S .

HTFT-derived hydrotreater feed is highly olefinic; therefore, at decomposition temperatures, in the absence of hydrogen and pressure, the possibility of feed polymerization and coke formation may not be ruled out completely.

3.4. Effect of Hydrogen and Nitrogen Pressure on Thermal Decomposition. It was postulated that applying high pressure may not be necessary during *in situ* thermal decomposition. The fact that thermal decomposition of prepared iron carboxylates was conducted at atmospheric pressure encouraged our investigation into the low-pressure decomposition studies. Sahdev reported that rust (Fe_2O_3) is converted to FeS in an oxygen-free atmosphere in the presence of H_2S or where the amount of H_2S gas exceeds that of oxygen (Scheme 2).²⁶ This has been previously noted in distillation columns and pressure vessels in oil refineries.

Scheme 2. Conversion of Rust into Iron Sulfide in the Presence of H_2S ²⁶



Using the above-mentioned information, it was speculated that the iron carboxylates in the hydrotreater feed are initially decomposed to iron oxides and then, under H_2S -rich

hydrotreating conditions, become converted to FeS , which tends to adhere more to the catalyst surface and cause bed plugging. Therefore, H_2S may not be directly involved in iron carboxylate decomposition but converts the iron oxides to sulfide.

Decomposition experiments were conducted in the absence of H_2S under a nitrogen blanket using commercial hydrotreater feed material. The pressure increased to 10 bar as the reactor temperature approached the decomposition temperature. Iron content analysis of filtered samples taken over a 90 min period showed a significant decrease in the iron concentration to ~ 2 mg/kg, comparable to those at high pressures (Figure 7).

However, those findings were under an inert atmosphere of nitrogen, and it was thus important to investigate if high-pressure hydrogen may assist during decomposition by reducing some of the dissolved iron carboxylates to form metallic iron ($\alpha\text{-Fe}$). Repeat experiments were conducted using the same feed at 300 °C and 50 bar hydrogen pressure. Iron content analysis of filtered samples showed a comparable decrease in the iron concentration with or without hydrogen, as depicted graphically below (Figure 7). Therefore, high-pressure nitrogen or hydrogen may have a negligible or no significant effect during thermal decomposition and removal of iron carboxylates. Hydrogen serves to prevent feed polymerization during carboxylate decomposition.

4. CONCLUSION

The acquired experimental evidence has shown that the foulant found in HTFT diesel hydrotreating units is the FeS precipitate

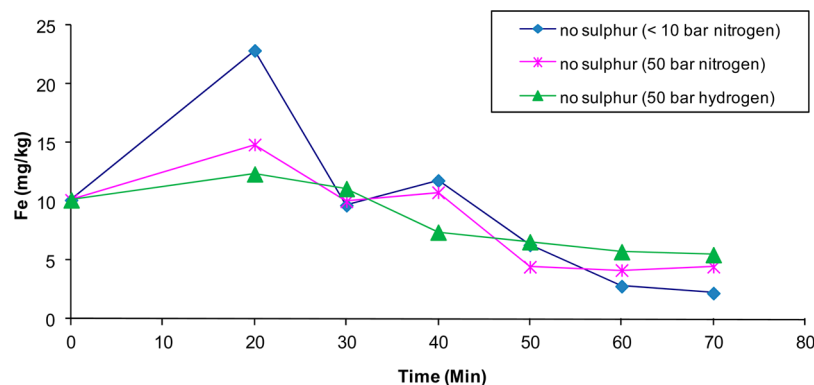


Figure 7. Analysis of the iron content in thermally treated and filtered hydrotreater feed material.

proposed to originate from iron carboxylates dissolved in the feed. Linear aliphatic C_5 – C_{11} Fe carboxylates believed to be major contributors to fouling have been successfully prepared, and our studies have confirmed that a reaction between carboxylic acids and iron follows a reactivity trend that decreases with an increase in the carbon chain length. This led to the formation of iron(III) carboxylates as elucidated by the Mössbauer spectroscopic technique. It is contemplated on the basis of our observations that HTFT diesel hydrotreater feed streams may contain similar species. It has been shown that the iron carboxylate decomposition process can be thermally controlled in such a way that the majority of iron carboxylates dissolved in the feed material can be decomposed at temperatures around 300 °C. An *ex situ* guard bed system operated at 300 °C may prove beneficial in the removal of the iron-based foulant arising from dissolved iron carboxylates and, thus, prolong the hydrotreating unit cycle length. Experimental findings demonstrate that iron carboxylates may be thermally decomposed *in situ* to form iron sulfide or iron oxide with or without H_2S , respectively. These studies have confirmed that around 300 °C is a critical temperature zone at which dissolved organic iron complexes decompose. It has also been shown that high-pressure hydrogen or nitrogen may not be necessary during thermal treatment and removal of the iron-based foulant.

■ ASSOCIATED CONTENT

● Supporting Information

Elemental analysis of the foulant samples (S1), XRD patterns of uncalcined and calcined crust samples (S2 and S3), FTIR spectra (S4–S10) and DSC calorigrams (S11–S17) of C_5 – C_{11} -prepared iron carboxylates, and table of decomposition temperatures (S18). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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