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Thiophene mitigates high temperature fouling of metal surfaces in oil refining

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HIGHLIGHTS

- Thiophene significantly reduces the fouling factor of heated metal in oil.
- Thiophene inhibits both sulfide and coke formation on metal surface.
- Inhibition originates from blockage of dehydrogenation reactions of other molecules.

ARTICLE INFO

ABSTRACT

Inorganically driven fouling of metal heat-transfer surfaces employed in crude oil refining operations is not well understood. The object of this study is twofold: First, we systematically elucidate the time-dependent mechanism of the interrelated carbonaceous and sulfidic build up that occurs at high temperatures on a metal surface (540 °C metal temperature, 250 °C oil bath temperature). Second, we demonstrate that additions of 0.5, 1.3 and 5.7 vol% thiophene (C_4H_4S) cause a 2×, 10×, and 20× reduction in the fouling factor after a 1400 min exposure. Analytical techniques including TEM, SEM–EDX, FIB, Auger electron spectroscopy and XRD were employed to detail the fouling phenomenology for a heated stainless steel wire immersed in atmospheric bottoms fraction crude oil, exposed for 1–1400 min. A key microstructural observation is the transformation of the wire's as-received near-surface textured austenitic grain structure into a micron scale (e.g. ~10 μm at 1400 min) highly porous inner-sulfide/chromium oxide bilayer composite. Additionally, we observe significant localized sulfidic attack into the bulk of the metal. During testing, an iron sulfide (pyrrhotite $Fe_{(1-x)}S$) corrosion product forms almost instantaneously at the metal surface, followed by coke formation around its periphery at longer times. This temporal sequence, combined with the observation that the thicker regions of the foulant are clearly associated with detached plumes of the sulfide, leads us to argue that the sulfide is essential for promoting organic fouling. This is brought about by the sulfide's action as a potent dehydrogenation catalyst that drives the transformation of pitch to coke. We hypothesize that the tremendous fouling inhibition effect of the thiophene originates from its adsorption onto the sulfide surfaces, thereby blocking the dehydrogenation reactions.

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1. Introduction

The growth of thermally insulating foulant in crude oil preheat trains, heat exchangers, fractionators and reactor beds continues to exude a high economic, industrial health and safety and CO_2 emissions impact in the refining industry. While delayed coking is the preferred technology for upgrading residue fractions, the requirement of a hot metal surface in contact with the oil means that thermal cracking and fouling are inevitable [1,2]. With the depletion of light sweet crude reserves comes the recognition that this will exacerbate due to the necessity of processing more asphaltenic and/or higher-sulfur crudes. Crudes derived from the Canadian

tar sands tend to demonstrate particularly severe fouling problems for refineries. Consequently asphaltene-flocculation driven fouling and coking behavior has been studied in great detail [3–33].

High-rate "catastrophic" fouling is brought on by large-scale asphaltene flocculation in incompatible oil mixtures and has been discussed in literature by Wiehe and coworkers [34–36]. For instance, recently researchers have employed multifunctional polyisobutenyl oxazolidines as stabilizers for asphaltenes with a great positive effect [37]. The nominally slower "chronic" fouling involves a gradual accumulation of organic and inorganic material on heated metal surfaces. This phenomenon may be broadly categorized into several mechanistic scenarios, which are not mutually exclusive. One scenario is particulate fouling by iron sulfide, where particles of sulfide form in the oil or boundary layer and deposit onto the hot metal surface, or into the coke layer. In this mechanism, the possibility of accelerated coking due to the presence of iron sulfide has been put forth [8,22,28]. The second mechanism is iron sulfide film fouling and involves the formation of an iron sulfide layer on the metal surface, followed by the deposition of coke [11,22,28]. Researchers have observed the presence of extensive iron sulfide in fouling deposits that were clearly not a result of particulate fouling [1,13,18,29]. The possibility of a catalytic effect of iron sulfide on coke formation is highly likely in either case. A third mechanism involves the formation of iron sulfide and coke simultaneously, brought about by the decomposition of the iron salts present in the oil [1,18]. The resultant carbonaceous deposit is observed to have a high concentration of iron sulfide particles throughout its bulk [18]. The contribution to fouling from in-situ chemical reaction processes still requires further elucidation [7,18,25].

The use of catalysts for heteroatom removal from heavy oils and during the upgrading of resids is ubiquitous [38,39]. Presently we will provide evidence that a catalytic phase also plays an important role during fouling reactions. The hydrodesulfurization (HDS) process is commonly catalyzed by a metal sulfide (usually molybdenum disulfide, MoS_2), which has been promoted with cobalt or nickel substitutional impurities and supported on a porous alumina pellet [40–44]. The mechanism for the HDS of thiophene (C_4H_4S) is a multi-step process involving the adsorption of the sulfur heteroatom onto a sub-coordinated edge site of MoS_2, followed by the scission of the C–S bonds [40,41,43]. A high partial pressure of hydrogen is critical to sustain the catalytic cycle and to liberate the adsorbed sulfur as H_2S [38,40,45]. Without hydrogen, the adsorbed organic sulfur atom is not released, and the catalytic site is blocked. The promoter impurities (nickel and/or cobalt) provide local regions of enhanced electron density along the MoS_2 edges, which result in lower binding energy and therefore higher activity for adsorption at the active site [41,43,46]. The role of iron as a promoter has also been characterized, and found to be effective, although much less so, than cobalt or nickel [41,46]. In addition to the effects of carbon supports on HDS [47], the efficacy of other catalysts such as iron sulfide [48,49] and coated stainless steel [50] have also been explored. Iron sulfide was proven to be an active catalyst for the HDS of thiophene, although much less effective than other sulfides such as MoS_2. Furthermore, it has been shown that metal surfaces [51], and an oxidized surface of a 304 stainless steel will embody some activity for the HDS of thiophene [50]. However, in the absence of hydrogen, thiophene is expected to be stable.

In catalytic upgrading it is well known that there are competitive reactions at work [52,53]. In general, the active site on a given catalyst can be poisoned by adsorbing polar species containing nitrogen or sulfur heteroatoms if there is not enough excess hydrogen to allow the catalytic cycle to continue [52,54]. These species adsorb readily onto active catalytic sites due to the polar nature of the molecules. Furthermore, it has been experimentally shown that the addition of thiophene and H_2S to a reactor has inhibitory effects on the catalytic cycle and the liberation of desired products [52]. There has also been some work on the role of thiophene in inhibiting coke formation during steam cracking of hydrocarbons and naphtha pyrolysis [55,56]. For the former case, the authors examined the formation of coke at 820 °C in reformer raffinate without thiophene and with 0.05, 0.1, and 0.5 wt% thiophene. It was observed that with increasing concentration of thiophene the rate of coking decreased significantly. The authors argued that thiophene both influences the radical conversion in the homogeneous phase and the surface reactions in the reactor, but this reaction mechanism was not proven. An early study by Taylor et al. demonstrated an inhibitory effect on foulant growth due to 3000 ppm (sulfur) of thiophene being added to deoxygenated jet fuel that was heated through a temperature range of 150–649 °C [57]. This was attributed to the thermal stability of the molecule, which resists pyrolysis and surface catalyzed decomposition reactions even at high temperatures.

Here we explore two key interrelated issues. First, the full phenomenology of chronic fouling in the absence of up-stream particulates is not yet entirely established. Evidence does exist that such chronic fouling is in fact a synergistic sulfidic corrosion-coke formation process [29]. However, factors like the evolution of both the foulant and of the underlying steel structure, as well as the overall uniformity versus any site-specificity of the process, are poorly understood. Thus our first goal is to provide a detailed and comprehensive account of the key microstructural changes that occur both in the heated metal and in the organic/inorganic deposit through a broad spectrum of exposure times. Second, we will provide direct evidence that the addition of thiophene to the oil may be employed to mitigate chronic fouling. This observation should serve as a useful basis for improved fouling mitigation strategies and antifouling additives.

2. Experimental procedure

A stirred 2000 mL autoclave was equipped with a heated wire probe. A detailed schematic is presented as Fig. S1. The reactor assembly allows for the immersion and resistive heating of wires in crude oil under repeatable reactor conditions. The autoclave reactor was designed for batch operation, with a single charge of 1200 mL of crude oil. Thiophene (C_4H_4S) was introduced into the autoclave as an oil additive to evaluate its effects on fouling. In these tests, 6 mL (0.5 vol%), 16 mL (1.3 vol%) and 68 mL (5.7 vol%) of thiophene were added to the oil. The resulting oil sulfur content increased by approximately 7%, 20%, and 80%, respectively. Fouling runs with thiophene were conducted for up to 1400 min, with fresh oil being used for each run. Prior to testing, the reactor was sealed, purged with nitrogen, and pressurized to 8.84 atm. For all tests the autoclave temperature was held 250 °C, while the pressure was adjusted to 15 atm prior to the start of the fouling run. During testing the oil was stirred using a stir bar rotating at 300 RPM.

The crude oil sample used for this study was an atmospheric bottoms fraction (nominally 340 °C+). Elemental analysis was conducted on the crude oil using a standard inductively coupled plasma mass spectrometry technique. The total acid number (TAN) of the crude oil was determined in accordance with ASTM standard D664-09a, using a Metrohm TIAMO 1.3 titration analyzer. Thermogravimetric (TGA) analysis of the crude oil and coke material was conducted using a Thermo Cahn TherMax 300 TGA analyzer. Micro carbon residue content was determined in accordance with ASTM standard D4530. CHNS analysis of the crude oil and coke was completed using a Carlo Erba EA1108 elemental analyzer. Asphaltene content of the crude oil was determined via standard precipitation analysis using pentane mixed at a ratio of 40:1 and