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Differential scanning calorimetric study of heavy oil catalytic oxidation in the presence of manganese tallates

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ABSTRACT

Metal tallates are attracting increasing interest in thermal enhanced oil recovery. Biodegraded heavy oil catalytic oxidation was investigated in the presence of manganese tallates. Differential scanning calorimetry (DSC) was used to highlight the effect of manganese tallates on the oxidation of heavy oil. The obtained data have been performed using the Kissinger method based on the isoconversional principle. Strong evidence of manganese tallates effect on heavy oil oxidation was illustrated in the high temperature oxidation region (HTO). The obtained catalyst increased constant rate in this region almost three times more than when reactions occur in its absence. We believe that we have found an innovative and economical solution to enhance heavy oil via in-situ combustion.

KEYWORDS

catalysts; heavy oil; in situ combustion; isoconversional-methods; non-isothermal analysis; oxidation; thermal analysis; Volga-Ural basin

1. Introduction

Despite the obvious advantages of in-situ combustion, it still has limitations associated with combustion front stabilization due to various factors. Oil bank formation during the process blocks gas flow leading to low displacement efficiency and to incorrect oxygen distribution because of low viscosity and result an early gas breakthrough (Shen 2002). Laboratory tests in combustion tubes have confirmed that when negative temperature region (NTO < 350 °C) reactions dominate the process, only small fractions of oil can be displaced and restored but in the case of HTO reactions domination, recovery tends to be very effective. Therefore, maintaining HTO reactions during in-situ combustion process is the main key to stabilize combustion front and hence to perform the efficiency of heat generation and displacement (Alexander, Martin, and Dew 1962).

Recently, catalytic in-situ combustion has been proposed as a promising alternative to the traditional in-situ combustion method (Ramirez et al. 2007). To stabilize the combustion front, it is believed that transition metals can play an important role as a catalyst for the process due to their availability, low price and positive environmental effects. Many studies have reported the use of transition metals as water-soluble salts, organometallic catalysts, or as nanoparticles to catalyze in-situ combustion (Kong and Ohadi 2010).

The efficiency of oil soluble catalysts is directly related to the metal part which plays the role of catalytic agent and to the organic part responsible for its solubility in the oil. Various highly soluble and ultrafine organometallic catalysts obtained from either acetylacetonate and alkylhexanoate compounds based on molybdenum, cobalt, nickel, iron and manganese were studied during the oxidation of heavy and super heavy oils (Ramirez et al. 2007). The results showed an increase

in oil production, a decrease in sulfur content and faster combustion front in the presence of catalysts compared to non-catalytic combustion.

Among the aforementioned metals manganese is recognized as being a promising catalyst-base to enhance both complete and partial oxidation of organic compounds. Its high catalytic activity, multiple oxidation states and low toxicity distinguish it from catalysts based on other transition metals. Galukhin et al. (2016, 2017) investigated the effect of a highly soluble manganese acetylacetonate and further confirmed the effect of manganese species by studying manganese sub-microparticles effect on heavy oil oxidation process using thermal analysis. The studies showed that manganese species accelerate predominantly high temperature oxidation process by increasing reactions rate in this region. However, using a number of high oil soluble catalysts might not be transferable to real application whether because of their high cost or their deficiency.

Tall oil is well known to improve oil composition in thermal processes (Feoktistov et al. 2018; Mikhailova et al. 2018; Sitnov et al. 2018; Vakhin et al. 2018a, 2018b). It is composed mainly of resin acids (50%); fatty acids (40%) and some unsaponifiable material and high molecular weight aliphatic alcohols. Tall oil also can be an economical effective raw material for obtaining highly effective organometallic catalysts for the process of heavy oil oxidation due to its high solubility in oil and its ability to inhibit asphaltene fluctuation (Feoktistov et al. 2018).

This research has tended to focus on the use of manganese tallates rather than other organo-manganese catalysts in heavy oil oxidation because of their economic and environmental effect. The aim of this study is to widen our knowledge about catalytic heavy oil oxidation in porous media. We applied differential scanning calorimetry to investigate the impact of tallates based catalyst on the process of heavy oil oxidation. It has been found that manganese tallates is a good candidate to enhance oil oxidation by increasing the high temperature oxidation constant rate and hence getting more stable combustion front which leads to a successful process.

2. Experimental

2.1. Materials

The crude oil (13.8 API°) adopted in this research was extracted from Ashalcha oilfield (Volga-Ural basin, Republic of Tatarstan, Russia). Organic solvent (dichloromethane - pure more than 99.5%), was supplied from Component Reactive and used without additional purification. Inorganic salts and pure quartz sand fraction of 43–64 μm were purchased from Sigma-Aldrich.

2.2. Samples preparation

Manganese tallates were prepared to a well-known method (Feoktistov et al. 2018) with some modifications. Samples for DSC analysis were prepared by mixing heavy oil (10.0 wt %) with pure quartz sand fraction of 43–64 μm , ([90.0– ω] wt %). In the case of catalytic experiments, initial oil sample contained 2 wt % of manganese tallates.

2.3. Thermal analysis

Differential scanning calorimetry (DSC) experiments were performed by means of STA 449 F1 Jupiter (Netzsch) thermoanalyzer in a temperature range of 30–600°C. The experiments were conducted at linear heating rates of 5, 10, 15, 20 K \times min^{−1}, under air flow of 50 ml \times min^{−1}. The obtained curves were processed by Proteus Analysis v5.2.1, NETZSCH Peak Separation (version 2010.09), and NETZSCH Thermokinetics 3.1 (version 06.08.2014) program packs.

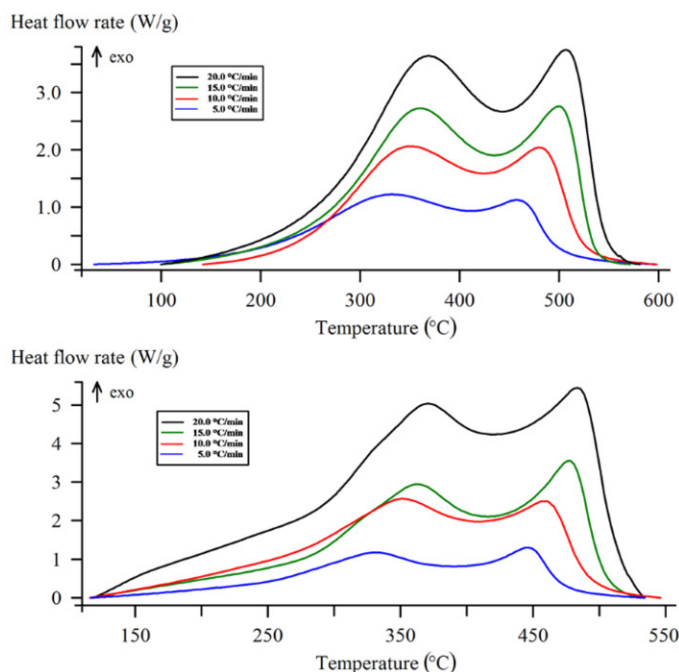


Figure 1. DSC curves for non-catalytic (top) and catalytic (bottom) heavy oil oxidation.

3. Results and discussions

Differential scanning calorimetry (DSC) presents a less time consuming and less expensive approach. Its application allows to estimate catalytic performance of manganese tallates. A pure quartz sand mixed with heavy oil sample was utilized as a reference sample. Figure 1 shows DSC curves for non-catalytic and catalytic heavy oil oxidation. Changes in peak temperatures were identified between the catalytic and no-catalytic oxidations for the two main oxidation regions, namely low temperature oxidation (LTO) and high temperature oxidation (HTO). It is commonly believed that LTO yields in oxygenated hydrocarbons (peroxides, alcohols, carbonyl compounds) without producing significant amount of carbon oxides, while HTO is usually described as coke oxidation producing carbon oxides and water (Sarathi 1999). Figure 1 illustrates the effect of adding a pre-catalyst especially on HTO region. It is evident that the catalyst has affected the high temperature region in the catalytic process by shifting the peak temperature to low values comparing to non-catalytic process. In the low temperature oxidation, the catalyst didn't play an important role as the figure shows negligible peak shifting between the catalytic and non-catalytic processes. DSC reaction intervals of both regions for non-catalytic and catalytic processes as well as peak temperatures are given in Table 1. We believe that this temperature shifting (Figure 2) is related to the effect of the pre-catalyst on the oxidation process. This matches and also confirms our earlier findings about manganese catalytic effect on high temperature oxidation (Galukhin et al. 2016, 2017).

Oil oxidation belongs to heterogeneous multiphases processes in which reaction rate is usually described as a function of conversion degree α , and oxygen partial pressure (Sarathi 1999). The values of α can be found by using DSC peak fractional areas.

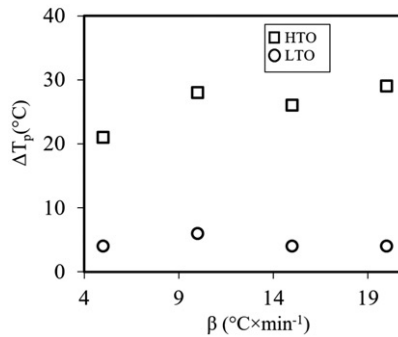
$$\frac{d\alpha}{dt} = k(T)P_{O_2}^a(1-\alpha)^b \quad (1)$$

The rate constant $k(T)$ is assumed to obey the Arrhenius law (Eq. 2):

$$k(T) = Ae^{-E/RT} \quad (2)$$

Table 1. DSC reaction intervals and peak temperatures

Sample	β , °C×min ⁻¹	Non catalytic		Catalytic	
		Interval, °C	T_p , °C	Interval, °C	T_p , °C
LTO	5	234–369	324	277–406	328
	10	270–379	343	312–392	349
	15	340–398	354	339–397	358
	20	349–409	363	349–405	367
HTO	5	397–486	472	425–466	451
	10	459–510	493	438–483	465
	15	481–527	506	450–500	480
	20	494–537	515	454–510	486


Figure 2. Differences between the peak temperatures (ΔT_p) of non-catalytic and catalytic heavy oil oxidation in porous media for low and high temperature oxidation at different heating rates.

In their work, Ramey et al. (Fassihi, Brigham, and Ramey Jr 1984; Bousaid and Ramey Jr 1968) showed mostly a first-order dependency of oil oxidation rate with respect to oil concentration and oxygen partial pressure. DSC is a method that uses small amount of oil to study (about 1 mg to each run) and high air flow rate of 50 ml/min combined with large furnace volume (approx. 250 ml) this is why we believe that oxygen partial pressure is constant during the experiment. Therefore, Eq. 2 transforms to its final reaction model as:

$$\frac{d\alpha}{dt} = k_{eff}(1-\alpha) \quad (3)$$

where $k_{eff} = kP_{O_2}$

The Kissinger's method (Kissinger 1956) was the best alternative to apply since it expresses process kinetic parameters as a function of peak temperature at different heating rate which are almost independent on the baseline choice and peak profile. Its logarithmic form is presented by Eq. 4. Kissinger's method also inherently assumes first-order dependence of reaction rate on $(1-\alpha)$, which is consistent with the chosen kinetic model (Eq. 3).

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{R} \times \frac{1}{T_p} + \ln(Af'(\alpha)) \quad (4)$$

Figure 3 shows Kissinger's plots for non-catalytic and catalytic processes of heavy oil oxidation. The kinetic parameters are grouped in Table 2.

Equation 2 shows the strong dependence of rate constants $k(T)$ on A and E_a parameters in both LTO and HTO processes. Therefore, we calculated rate constants values $k(T)$ in these regions to estimate the total effect of these two parameters. The Comparison of effective rate

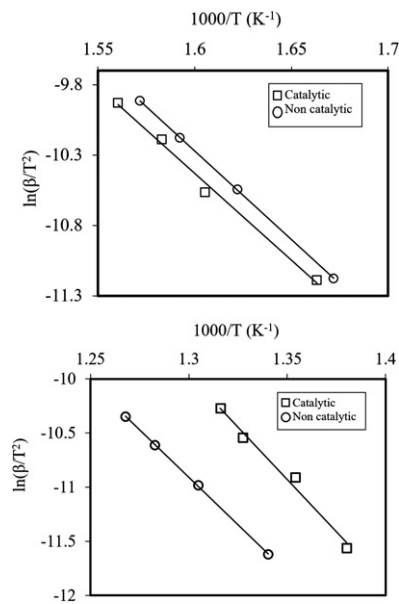


Figure 3. Kissinger's plots for catalytic and non-catalytic high temperature oxidation (top is for LTO, bottom is for HTO).

Table 2. Kinetic parameters of oxidation processes

	Non-catalytic		Catalytic	
	LTO	HTO	LTO	HTO
E_a , kJ/mol	104.6 ± 1.6	145.8 ± 8.5	103.4 ± 1.6	163.3 ± 8.1
$\log_{10}A$, A in min ⁻¹	9.4	11.8	9.8	15.1

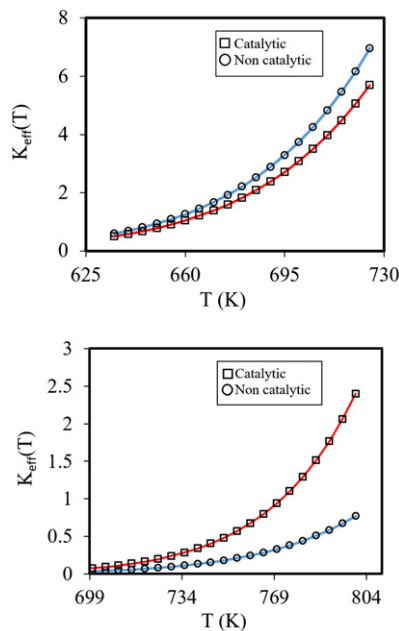


Figure 4. Variation of effective rate constants with temperature for catalytic and non-catalytic oxidation (top is for LTO, bottom is for HTO).

constants for non-catalytic and catalytic oxidation processes is presented on Figure 4 where the difference is quite clear between non-catalytic HTO and catalytic HTO because of the wide difference in E_a and A values of this region. In LTO region, the difference is almost absent since E_a and A variation is minimal for both processes.

4. Conclusions

Our work has led us to conclude that tallates can be an economical and a potential base for catalytic heavy oil oxidation processes. The evidence from this study points toward the idea of the important use of manganese based on tallates to enhance heavy oil recovery via in-situ combustion. We applied DSC analysis and non-isothermal kinetic analysis to study the influence of catalyst on heavy oil oxidation process by calculating the related kinetic parameters. The obtained catalyst increased constant rate in HTO region almost three times more than when reactions occur in its absence. Our research has highlighted the excellent catalytic performance of the obtained manganese tallates on the process of heavy oil oxidation. It provides an encouragement for a new way to emphasis on using tallates with other transition metals to get further improvements in enhancing oil recovery field.

Disclosure statement

The authors declare that there is no conflict of interests regarding the publication of this paper.

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