Comparative Kinetic Study on Heavy Oil Oxidation in the Presence of Nickel Tallate and Cobalt Tallate

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ABSTRACT: A remarkable feature of heavy oil oxidation during the in situ combustion process is the difficulty in maintaining combustion front to flow throughout the reservoir. Recent developments suggest the use of catalysts regarding this issue. Previous works have been limited by the catalyst choice. Moreover, many research works have failed to provide a catalyst that meets the requirements of efficiency, low-cost, and positive impact on the surrounding. This paper presents new type of catalysts based on tallate, each combined with nickel and cobalt, respectively, as highly efficient catalysts for the oxidation of heavy oil. We have compared the effect of each catalyst using differential scanning calorimetry to highlight kinetic parameters of each process by the Kissinger method. In addition, we employed thermogravimetric analysis and scanning electron microscopy to investigate the behavior of catalysts during the process. The obtained results showed a similar high efficiency of both precatalysts by decreasing the activation energy of the high-temperature oxidation region, increasing the preexponential factors of both high- and low-temperature oxidation regions, and increasing their reaction rate constants. Moreover, the precatalysts used transformed in situ to nanoparticles during the heavy oil oxidation process.

1. INTRODUCTION

Unconventional oil resources are attracting considerable interest due to the shortage of conventional fossil fuel resources as a result of market demand growth associated with population expansion.[1] Traditionally, the focus has always been on conventional oil resources, while unconventional oil resources have been less exploited. This less exploitation of unconventional oil resources is related to their costly and hard extraction from reservoirs with complicated structures. Among unconventional oil resources, heavy and extra-heavy oils are set to become an alternative vital factor in terms of maintaining demand satisfaction for further decades at least.[2] These types of oils present more than 40% of fuel resources on the earth.[3] Early studies on the characteristics of heavy and extra-heavy oils have focused on their high viscosity and density, which are the main cause of their difficult exploitation. In their work[4] Abrams et al. have studied the influence of viscosity on oil recovery factor and have shown that the oil recovery factor decreases with the increase of oil viscosity. Various approaches and methods have been proposed to solve this issue known as enhanced oil recovery (EOR) methods.[5,6] These methods are considered as an efficient approach for exploiting unconventional oil resources. They are based on introducing an external agent into the reservoir to change oil characteristics in situ, and consequently, its extraction becomes feasible.[7] EOR methods are classified into different types according to the applied technique adapted like chemical,[8] electrical,[9] and thermal[10] methods. A growing body of literature has investigated the potential of thermal enhanced oil recovery methods and demonstrated their effectiveness compared to other types of enhanced oil recovery methods.[10−13] What we know about thermal enhanced oil recovery methods is that they are generally a type of techniques that apply heat on oil to decrease its viscosity, hence increasing its mobility and flow.[10] Hyne et

al. have studied the aquathermolysis of heavy oil in reservoir conditions and found that the process improves oil quality.[14] Other works[15] have also showed the good efficiency of polymer and surfactant flooding in decreasing heavy oil viscosity. However, one of the major drawbacks in using these methods is the high cost related to their application in addition to the insufficient amount of the recovered oil.[16] In situ combustion since then has been gaining much attention due to the positive economic and environmental impacts that could be generated from its application in heavy and extra-heavy oil reservoirs.[17−19] The idea of in situ combustion is generally based on injecting air into the reservoir to initiate combustion under reservoir conditions (generally high temperature and high pressure). By burning a portion of the reservoir crude oil, heavy oil gives birth to a combustion front due to the generated exothermic reactions.[20] However, various attempts have been implemented for the extraction of heavy and extra-heavy oils using this method, but unfortunately they faced several problems and drawbacks.[21] A few projects using in situ combustion to extract heavy oil have been successfully applied like the Romanian field project.[22] As a result, combustion front has been identified as the main part in the in situ combustion process since the quantity of the recovered oil is dependent directly on its flow through the reservoir.[23] Thus, stabilizing combustion front is a crucial feature that should be well studied and solved for successful implementation of this process.[24]

Different hypotheses have been proposed to solve this issue. However, the use of catalysts is considered a promising way for improving the efficiency of the process by stabilizing and

promoting its combustion front.[25] It is generally accepted that transition metal-based catalysts play an important role in the modern industry and in a wide range of oil refining and petrochemical processes.[26] He et al. have applied different water-soluble catalysts in the in situ combustion process of heavy and light oil and have studied their impact using a combination of combustion tubes and ramped temperature oxidation experiments.[27] The results highlighted the potential effect generated from the presence of this kind of catalysts in the in situ combustion process where they have decreased the activation energy of reactions occurring and increased the oxygen consumption. Other works[28−32] have been performed on heavy oil oxidation in the presence of particle catalysts in micro- and nanosized forms and have also showed their crucial effect on decreasing the activation energy of the process of high-temperature oxidation (HTO).

Regardless of the good efficiency of the aforementioned types of catalysts in the oxidation of heavy oil at laboratory scales, their application in real field tests is still limited. On the one hand, the terraces of different crystal structures, edges, steps, additives, impurities, and defects associated with any practical catalyst make its sites heterogeneous and thus lead to a nonuniform catalytic surface.[33] Therefore, a good knowledge of the reaction mechanisms on each site becomes hard to understand. On the other hand, a practical challenge may be expressed by the difficulty in reaching a uniform dispersion of catalysts in the reservoir oil surface, especially for water-soluble catalysts. Moreover, the injection of microparticles and nanoparticles into the reservoir and their dispersion within the reservoir are difficult tasks.

Applying oil-soluble catalysts may be a potential solution for catalyst injection into the reservoir and may implement high dispersion. Ramirez-Garnica et al.[34] studied heavy oil oxidation (12.5 °API) in the presence of a nickel-based oil-soluble catalyst using combustion tube experiments that has improved the process kinetic parameters as well. Our previous work on studying the mechanism of manganese acetylacetonates catalyst in heavy oil oxidation[35] has highlighted a good dispersion in the medium and led to improvement of reaction kinetics. During the process at different temperatures, manganese acetylacetonates (III) has transformed to manganese acetylacetonates (II) passing by Mn_3O_4 and at the end of the reaction has transformed to Mn_2O_3, as shown in Figure 1.

The fundamental characteristics of transition metals are their availability, efficiency in catalytic processes, and their ability to change their oxidation state in addition to their low price relative to other metals. All of these properties attract con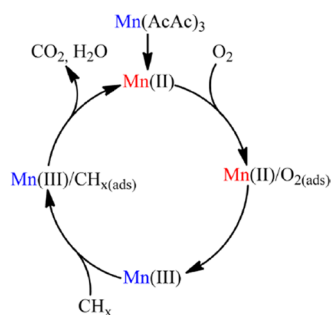siderable interest in terms of their application in the process of in situ combustion to solve combustion front features.[26]

Nickel is one of the widely used metals for obtaining effective catalysts of oxidation. It has been used in different processes like an agent for enhancing asphaltene sorption during their oxidation.[36] Its combination with tallate results in a highly oil-soluble catalyst capable of dispersing completely in heavy oil medium and facilitates the reaction of its components with air. Adding to this, nickel is considered a multivalent metal, which is thermally resistant and may change its properties with the increase in temperature.[37] Another metal very effective as nickel and proposed to be used in in situ combustion is cobalt.[38] It possesses similar properties to nickel in terms of catalytic and behavioral aspects.[39] The combination of the aforementioned catalyst with tallates is a promising way to guarantee a high dispersion extent of catalytic agents during the oxidation process, as have been demonstrated in our previous works on iron[40] and manganese tallates.[41]

This paper aims to validate our previous finding[40,41] about the utility of using oil-soluble catalysts based on tall oil in the in situ combustion process. Thus, we have studied the effect of heavy oil oxidation in the presence of nickel tallate and cobalt tallate as effective precatalysts for enhancing the oil oxidation process. According to the obtained results, both nickel and cobalt tallate may be good catalysts for the process of heavy oil oxidation in terms of economic, time consuming, and positive impact on environmental by improving oil quality. However, cobalt tallate showed a slightly better effect on enhancing the process effective rate constant during HTO compared to nickel tallate.

2. EXPERIMENTAL SECTION

2.1. Materials. We used a sample of biodegraded heavy oil extracted from Ashalcha oilfield (Volga-Ural basin, Republic of Tatarstan, Russia) as an object of study. Its physical properties are presented in Table 1.

Since the heavy oil used in this study exists at a relatively inconsiderable depth (about 300 m), it is supposed to cause biodegradation, as indicated by its saturated fraction GC−MS chromatograms in Figure 2 where it can be seen that the amount of alkanes is relatively low, which is explained by the biological effect of bacteria on alkane consuming (the number on peaks present the total number of carbon atoms in alkanes).
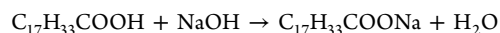
Organic solvents of purity greater than 99.5% have been purchased from Component Reactiv and used without further purification.

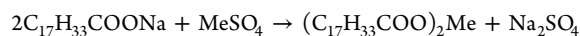A sand fraction (43−64 μm) with inorganic salts have been purchased from Sigma-Aldrich.

2.1.1. Sample Preparation. We used a reliable method based on the recommendations of Feoktistov et al.[42] to obtain cobalt tallate. By an analogical method, we obtained nickel tallate.

The method of obtaining precatalysts based on nickel and cobalt is a simple reaction of distilled tall oil saponification followed by a reaction with metal salts at 75−80 °C for about 3 h as follows.

Saponification

$$C_{17}H_{33}COOH + NaOH \rightarrow C_{17}H_{33}COONa + H_2O$$

Metal salt addition

$$2C_{17}H_{33}COONa + MeSO_4 \rightarrow (C_{17}H_{33}COO)_2Me + Na_2SO_4$$

where Me is the metal (Ni or Co).

For the noncatalytic oxidation, we have prepared a mixture of heavy oil (10.0 wt %) with a pure quartz sand fraction of 43−64 μm (90.0 wt %). For the catalytic process, 2 wt % catalyst (cobalt tallate or nickel tallate) was present in the initial sample of oil.

2.2. Thermal Analysis. Differential scanning calorimetry (DSC) and thermogravimetric (TGA) experiments have been considered

Figure 1. Catalytic cycle of Mn(AcAc)₃ in heavy oil oxidation.[35]

Table 1. Physical Properties of Ashalcha Heavy Oil at 20 °C

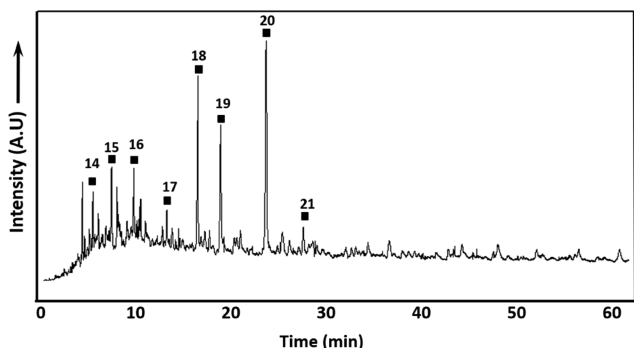|			elemental content, %				SARA analysis, %			
viscosity, mPa × s	density, g × cm⁻³	API gravity	C	H	N	S	saturated	aromatic	resins	asphaltenes
11 811	0.97	13.8	83.45	10.29	0.36	3.8	34.3 ± 0.5	34.2 ± 0.6	25.2 ± 0.5	6.3 ± 0.3

Figure 2. GC−MS chromatograms of the saturated fraction of the biodegraded oil sample.

appropriate methods to use in this study, and they have been realized on a STA 449 F1 Jupiter (Netzsch) thermoanalyzer at a temperature range of 30−600 °C. The experiments were conducted at linear heating rates of 5, 10, 15, and 20 K × min⁻¹ under a 50 mL × min⁻¹ airflow. The obtained data were treated with care by Proteus Analysis v5.2.1, NETZSCH Peak Separation (version 2010.09), and NETZSCH Thermokinetics 3.1 (version 06.08.2014) program packages.

One of the major drawbacks in oil oxidation kinetic studies is the lack of knowledge about reactions occurring during the process, which exist in heterogeneous medium and are accompanied by the diffusion phenomenon. For this reason, many research works[43] consider the reaction rate of the process as a function of conversion degree, α, and oxygen partial pressure, as expressed by eq 1.

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

where α can be obtained from DSC peak fractional areas, b is the reaction order, and $P_{O_2}^a$ is the oxygen partial pressure.

The rate constant, $k(T)$, takes the Arrhenius law form as follows

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

In their works,[44,45] Fassihi et al. and Bousaid et al. have showed that oil oxidation reaction order is equal to 1 ($b = 1$) relative to oil concentration and oxygen partial pressure. A related hypothesis maintains that oxygen partial pressure is constant during DSC experiments due to the small size of the studied samples and the large furnace volume with high airflow, which may lead to

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

where $k_{eff} = kP_{O_2}$ and K_{eff} is the effective rate constant.

2.3. Kinetic Analysis. We chose Kissinger's method[46] for kinetic calculations since it is based on a simple approach to calculate the activation energy and preexponential factors by relating peak temperatures at different heating rates independently of baseline and peak profile choices. Kissinger's equation is presented by

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

3. RESULTS AND DISCUSSION

Thermal analysis has several beneficial applications in terms of estimating heat effects and mass loss during oil combustion. DSC is a less lengthy, rapid, and cheap method that may evaluate kinetic parameters of heavy oil oxidation. A more elegant solution for studying catalyst behavior and characterizing the obtained product at the end of the process is the combination of TGA with SEM.

DSC was used to predict the catalytic effect of both Ni tallate and Co tallate on the oxidation of heavy oil compared to its oxidation in the absence of these precatalysts. There was a significant positive correlation among peak temperature shifting in Figure 3, the results obtained in Table 2, and
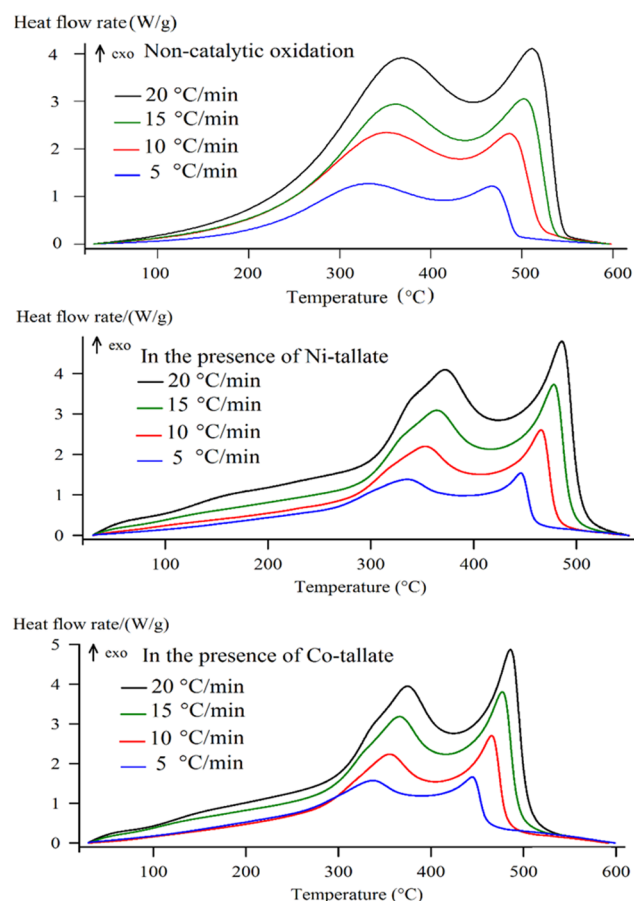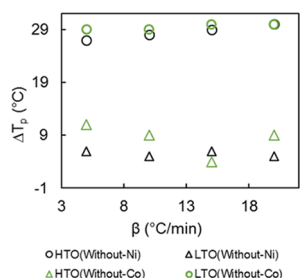

Figure 3. DSC curves for noncatalytic and catalytic Ashalcha heavy oil oxidation in the presence of Ni tallate and Co tallate.

peak temperature differences of heavy oil oxidation between both catalytic and noncatalytic processes in Figure 4. First, as shown in Figure 3, DSC curves take the same shape in all cases, as described in earlier works as low-temperature oxidation (LTO) for the first peak at low temperatures (230−390 °C) followed by high-temperature oxidation (HTO) for the last peak at higher temperatures (430−550 °C). However, a slight difference in low-temperature oxidation peak shifting at

**Table 2. DSC Reaction Intervals and Peak Temperatures**

sample	β, °C × min^{-1}	without catalyst		with Ni tallate		with Co tallate	
		interval, °C	T_p, °C	interval, °C	T_p, °C	interval, °C	T_p, °C
LTO	5	234−369	324	290−372	330	286−385	335
	10	270−379	343	314−383	348	316−389	352
	15	340−398	354	321−396	360	325−404	364
	20	349−409	363	340−405	368	335−410	372
HTO	5	397−486	472	434−455	445	430−455	443
	10	459−510	493	452−476	465	452−476	464
	15	481−527	506	464−489	477	461−489	476
	20	494−537	515	470−499	485	470−499	485

Figure 4. Differences between peak temperatures (ΔT_p) of noncatalytic and catalytic Ashalcha heavy oil oxidation in the presence of Ni tallate and Co tallate for low- and high-temperature oxidation regions at different heating rates.

different heating rates was observed between oil oxidation in the presence of Ni tallate and Co tallate and oil oxidation in their absence. However, this difference is more significant for the high-temperature oxidation region where peak temperatures at different heating rates shift considerably, especially in the presence of Ni tallate compared to Co tallate. These observations have been further confirmed by determining LTO and HTO region temperature intervals, as shown in Table 2, and by calculating peak temperature differences (ΔT_p) between noncatalytic and catalytic oxidations for low- and high-temperature regions at different heating rates (Figure 4).

The next step was the estimation of oil oxidation kinetic parameters to justify the acceptability of our findings. As hypothesized, Kissinger's plots of the oxidation of heavy oil in the presence and absence of Ni tallate and Co tallate for both LTO and HTO (Figure 5) highlight the role played by Ni
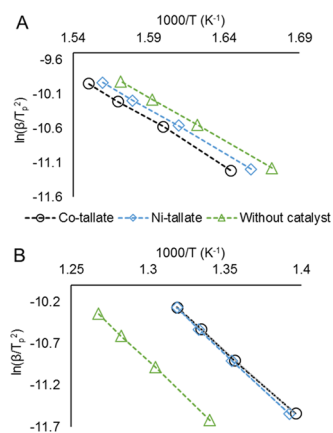
Figure 5. Kissinger's plots for catalytic and noncatalytic Ashalcha heavy oil oxidation (A is LTO, B is HTO).

tallate and Co tallate in shifting peak temperatures especially for high-temperature oxidation regions where there is a clear difference between the oxidation plots in the presence of Ni tallate (blue) and Co tallate (black) and in their absence (green). Based on Kissinger plots, we calculated kinetic parameters of each process, as shown in Table 3.

Initially, we thought that Ni tallate is significantly more effective than Co tallate according to peak temperature shifting, in Figure 2. However, a more careful analysis of obtained kinetic parameters in Table 3 has revealed that Co and Ni tallates have similar influence on the heavy oil oxidation process in terms of decreasing the activation energy of both low-temperature and high-temperature oxidation regions and increasing the preexponential factor. Thus, we proceeded to further calculations concerning oxidation reaction rates in the presence and absence of Ni tallate and Co tallate.

Figure 6 indicates exactly the oil oxidation effective rate constants in low- and high-temperature oxidation regions. There is a significant similarity in low-temperature oxidation effective rate constants, which is considered to be a positive effect since this indicates no change in the quantity of fuel obtained during the process that may prevent the inhibition of low-temperature oxidation region reactions.[47]

In contrast with the low-temperature oxidation region, we found much higher values of high-temperature oxidation reaction effective rate constants in the presence of Ni tallate and Co tallate compared to those in their absence. Nevertheless, the effect of Ni tallate and Co tallate is fairly similar, as shown in Figure 6 (bottom). We believe that this difference is related to the significant amount of asphaltenes and resins in oil compared to alkanes and aromatics as observed in the GC−MS analysis. Catalysts affect first the C−S and C−N bonds existing in asphaltenes and resins, leading to low molecular components especially at high-temperature oxidation at which occurs the formation of metal nanoparticles with a higher surface area on which the adsorption of asphaltenes and resins becomes more important.[48]

To study the reason behind the similarities of Ni tallate and Co tallate effects on heavy oil oxidation, we used thermogravimetric analysis to investigate the decomposition of Ni tallates and Co tallates with temperature raising from 30 to 600 °C at a 10 °C/min heating rate in addition to SEM. The TGA results of catalyst decomposition are represented in Figure 7.

As detailed in Figure 7, the Ni tallate thermogram and its DTA curve are in complete agreement with Co tallate ones in terms of shape and even in terms of decomposition degree where we can clearly observe that both precatalysts at higher temperatures (366 and 350.8 °C, respectively) lose the hole organic matter originating from tall oil surrounding the metal.

Table 3. Kinetic Parameters of Combustion Processes

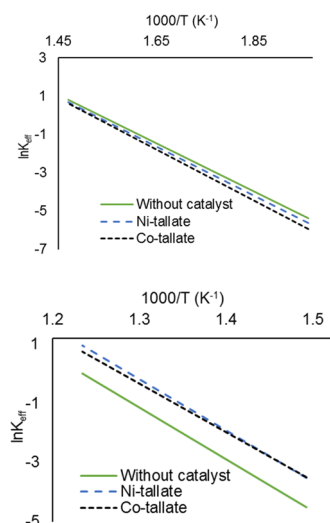|	without catalyst		with Ni tallate		with Co tallate	
	LTO	HTO	LTO	HTO	LTO	HTO
E_a, kJ/mol	104.6 ± 1.8	145.8 ± 8.3	106.4 ± 1.7	143.8 ± 8.5	111.2 ± 2.1	136.8 ± 7.3
$\log_{10}A$, A in min^{-1}	9.8	11.9	10.8	12.5	10.8	11.3

Figure 6. Variation of effective rate constants with temperature for catalytic and noncatalytic oxidation (top is for LTO, bottom is for HTO).
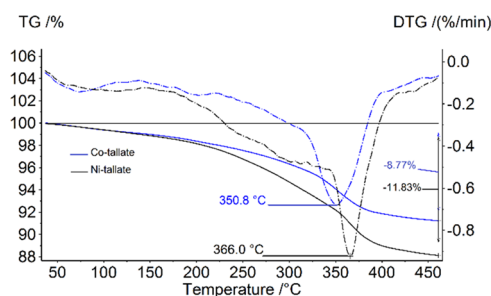

Figure 7. TG and DTG curves of the decomposition of Ni tallate and Co tallate.

Figure 8. SEM image of the obtained NiO_2 (top) and CoO (bottom) nanoparticles from the decomposition of Ni tallate and Co tallate at 400 °C.

We believe that at these temperatures metal oxide nanoparticles of Ni and Co form, and we suggest that they were the effective catalytic agents that catalyze in the high-temperature oxidation region. To confirm our hypothesis, we applied scanning electron microscopy on a sample of Ni tallates and Co tallates heated up to 500 °C for 4 h. SEM images of the obtained products, as shown in Figure 8, highlighted nanosized particles of NiO with an average size of 10 ± 5 and CoO with an average size of 20 ± 5 nm.

4. CONCLUSIONS

In this study, we have compared the catalytic effect generated by Ni tallate and Co tallate on the kinetic parameters of heavy oil oxidation. The evidence from this study suggests that Ni and Co tallates possess the same catalytic effect on the accelerating reaction rate especially in the high-temperature oxidation region and the difference between their influence on the activation energy and preexponential factor is almost negligible. Both precatalysts as a result enhanced the oxidation reaction effective constant rate by transforming in situ to
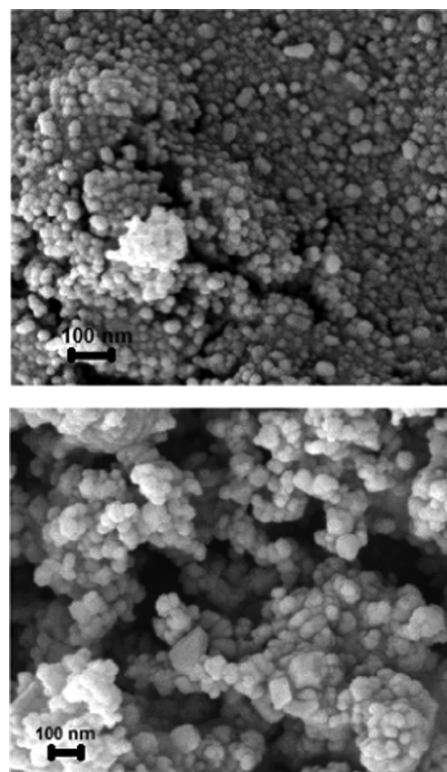
nanoparticles that have high efficiency due to the increase in surface area and thus more adsorption (more activity). However, considerable progress has been made in regard to catalytic heavy oil oxidation using tallates as an oil-soluble base. The present study has only investigated the kinetic parameters of the oxidation process and the characteristics of the product of catalyst decomposition using thermal analysis, which are mainly limited by the small size of the studied sample and the absence of reservoir conditions. Therefore, further studies taking in account the catalyst mechanism, high pressure, and the phenomenon of porous media should be performed in the future. We believe that the present findings have important implications for solving front combustion earlier breakthrough during the application of in situ combustion for enhancing heavy oil recovery.

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Notes

The authors declare no competing financial interest.

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