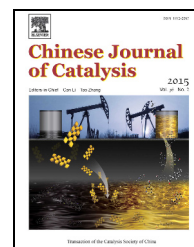


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## Article

# Controllable oxidation for oil recovery: Low temperature oxidative decomposition of heavy oil on a $\text{MnO}_2$ catalyst



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## ABSTRACT

Heavy oil is a readily available alternative energy resource with a reserve that is more than twice that of conventional light oil. *In situ* combustion is one of the most promising strategies for heavy oil exploitation, and the modulating of the oxidation behavior of heavy oil is an efficient way to expand the applicability of the *in situ* combustion method.  $\text{MnO}_2$  nanoparticles were employed to facilitate the cracking of heavy compounds, promote heat production, and improve recovery efficiency. The oxidative decomposition rate of heavy oil was doubled in the low temperature interval, and the heat release rate was accelerated in the high temperature interval. The increased weight loss at low temperature was attributed to the decomposition of heavy components. The detection of incomplete oxidation products by mass spectroscopy under excessive oxygen flow at high temperature indicated a diffusion controlled process of oil combustion. The same amount of  $\text{CO}_2$  from the combustion of less fuel demonstrated an increased oxidation degree of the products. The apparent activation energies of the oxidation reactions were decreased by 10–30 kJ/mol at low temperature and 20–40 kJ/mol at high temperature by the addition of  $\text{MnO}_2$ .  $\text{MnO}_2$  can render *in situ* combustion more feasible for various oil reservoirs, and is also promising for other thermal recovery processes for improved oil recovery.

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## 1. Introduction

Petroleum is the most important resource for fuels [1,2] and chemicals [3–5]. The reliance on petroleum is still growing [6] because of the absence of a good alternative substance. Consequently, the exploitation of heavy oil, whose reserve is over twice that of conventional oil, has received much attention in recent years. Thermal recovery methods have been widely employed to reduce its viscosity and to simplify its transportation. Among the various strategies, *in situ* combustion, which is based on the exothermic oxidative reactions of heavy oil, is a promising method [6].

The control of an *in situ* combustion process is a big challenge because of the different geological characteristics as well as complex properties of heavy oil [7–9]. Neither the recovery efficiency nor product quality can be accurately predicted. As a result, the broad application of *in situ* combustion is severely hindered. Much effort has been devoted to the better control of *in situ* combustion. Moore et al. [10] and Weissman et al. [11] first proposed the concept of a combination of *in situ* combustion with down-hole catalytic upgrading in the 1990s. The addition of a Ni/Mo/Al catalyst by Moore et al. [10] in combustion tube experiments induced significant hydrodesulphurization and a gravity increase from 15.3° to 21.2° API. Catalytic up-

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grading using a conventional hydroprocessing catalyst combined with a hydrogen source under similar conditions was investigated by Weissman et al. [11]. A 50% sulfur removal and an 8-point API gravity increase were obtained. Together with recent advances in controllable horizontal drilling, the catalytic upgrading process *in situ* (CAPRI) integrated with toe-to-heel air injection (THAI), collectively called THAI-CAPRI [12–15], was proposed, and a field trial has been implemented [16]. Nassar and co-workers [17] reported that water-in-vacuum gas oil microemulsions containing trimetallic (W, Ni, and Mo) ultra-dispersed colloidal nanoparticles penetrated into the porous medium, reacted with the bitumen and enhanced oil recovery. In addition to the investigations on improving product quality, the extension of its application to reservoirs with various APIs has also attracted much attention since the API of the oil affects the performance of this technology. In light reservoirs [18], it is difficult to achieve the desired high temperature region to ensure a self-sustaining process because not enough fuel is available for combustion, while in heavy reservoirs, excessive fuel is deposited and combusted resulting in uneconomical exploitation [19]. Therefore, if heat production by combustion was enhanced or the cracking of heavy compounds at low temperature was promoted, fuel deposition for combustion will rely less on the property of the oil. Then, the *in situ* combustion can be controlled to be within an appropriate range, and is suitable for a wider variety of oil reservoirs.

Solid catalysts with extraordinary performance and multi-functions [20–22] have been employed to modulate the oxidation behavior of heavy oil [23,24]. Castanier's group [25–29] proposed water soluble metallic additives as catalyst to modify the fuel deposition reactions and to increase fuel laydown for light oils. This has been successfully applied in fields in Hungary [30] and Niemangu [31] in China. However, suitable additives for reducing fuel deposition have not been reported until very recently when Babadagli and coworkers [32] found that nickel ions had a significant effect on the low temperature reactions and increased the amount of mass loss by 10% at 300 °C, whereas this effect was not observed at 200 °C. A shift of the LTO products from oxygenated compounds to CO<sub>2</sub> and H<sub>2</sub>O was also detected. Unfortunately, the catalytic effect on the kinetics and products and the heat-release performance of nickel ions was not fully illustrated in the work. Since heat is the most important factor for the thermal recovery method, the evaluation of heat release is critical, especially when the amount of fuel deposition is decreased. An additive is applicable only if it has no negative impact on the heat generation of oil combustion at high temperature. With a catalyst that promotes the cracking of heavy compounds at low temperature and enhances the heat production of the residue at high temperature, the *in situ* combustion process would give higher recovery efficiency and have wide applications in various oil reservoirs.

In this contribution, a metal oxide catalyst, MnO<sub>2</sub>, was used to facilitate the cracking of heavy compounds at low temperature and to enhance the heat-release rate at high temperature. In addition to the weight loss performance, special attention was also paid to the change in thermal effect and representative product concentrations due to the addition of the catalyst.

The reason we selected MnO<sub>2</sub> as the metal oxide catalyst was because of its excellent catalytic oxidation performance at low temperature [33–36]. The MnO<sub>2</sub> nanoparticle catalyst was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The distributed activation energy model (DAEM) was employed to describe the kinetic behavior of the catalytic oxidation of heavy oil. This method is expected to modulate the oxidation behavior, regulate the oxidation characteristics of a crude oil, improve the quality of the produced oil, and enhance oil recovery.

## 2. Experimental

### 2.1. Feedstock

The heavy oil used was obtained from Xinjiang Oil Field. The properties and elemental analysis of the heavy oil are listed in Table 1. The crude oil was separated from the sand to eliminate catalytic effects arising from inorganic compounds. It was subsequently devolatilized under an inert atmosphere at 300 °C for 3.0 h to eliminate the influence of light component volatilization on weight loss and the heat flow profiles prior to oxidation experiments.

The MnO<sub>2</sub> catalyst was obtained from Alfa Aesar. The mixture of MnO<sub>2</sub> and heavy oil was obtained by the following steps. First, MnO<sub>2</sub> nanoparticles were introduced into the heavy oil under vigorously mechanical stirring in an oil bath held at 80 °C to give an amount of 0.1 wt%. Second, the mixture was continuously stirred for 1 h, and then further treated in an ultrasonic bath at 50 °C for another 0.5 h. Finally, the mixture was transferred to a ceramic boat to devolatilize the light component under Ar at 300 °C for 3.0 h.

### 2.2. Catalytic oxidation of heavy oil

Thermal gravimetric analysis (TGA, Mettler Toledo, TGA/DSC 1) under an O<sub>2</sub> atmosphere was carried out to investigate the oxidation performance of the heavy oil and the catalytic activity of the MnO<sub>2</sub>. The mass change and heat flow were measured in a temperature range of 30–550 °C with a ramp rate of 5 °C/min and a feed rate of 90 ml/min. The gas phase product evolved from oil oxidation were sampled into a mass spectrometer (MS, Hiden, QIC-20) by a capillary tube heated at 200 °C to measure the profiles of typical products and evaluate the catalytic effect of the MnO<sub>2</sub> catalyst. Since the concentration of each product in the gas phase was very low, a secondary electron multiplier (SEM) detector was employed to improve the measuring accuracy. The products were identified by their molecular fragment ions at different mass-to-charge ratios

**Table 1**

Physical properties and elemental analysis of the heavy oil from Xinjiang Oil Field.

Density (g/cm <sup>3</sup> , 25 °C)	Viscosity (mPa·s, 50 °C)	Elemental analysis (wt%)					
		C	H	N	S	O	H/C
0.96	18000–28000	85.18	12.45	0.83	0.39	1.14	1.75

( $m/z$ ). The  $m/z$  values of 15, 18, 43, and 44 were used for  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_3\text{H}_8$ , and  $\text{CO}_2$ , respectively. The same experiment was repeated at least twice to ensure repeatability and accuracy.

### 2.3. Catalyst characterization

The morphology of the catalyst was determined by a JEM 2010 TEM (JEOL Ltd., Japan) equipment operated at 120 kV. The crystal phase of the catalysts was determined by wide angle XRD on a D8 ADVANCE Rigaku D/max-RB diffractometer (Bruker, Germany) using  $\text{Cu K}\alpha$  radiation at a voltage and current of 40 kV and 120 mA. The chemical state of the elements on the surface of the catalyst was identified by XPS on an ESCALAB 250Xi spectrometer using  $\text{Al K}\alpha$  as excitation source. The binding energies (BEs) of the Au 4f, Mn 2p, and O 1s were calibrated against the C 1s signal (284.6 eV) of contaminant carbon.

## 3. Results and discussion

### 3.1. Morphology and electronic structure of the $\text{MnO}_2$ catalyst

As observed in Fig. 1, the  $\text{MnO}_2$  catalyst displayed a high crystallinity of the  $\beta\text{-MnO}_2$  phase (JCPDS 44-0141). No diffraction peak from an impurity was detected. Irregular shapes and a polycrystalline structure with rough edges were observed in the high resolution TEM images (Fig. 2).

The chemical state of the O and Mn species on the surface of  $\text{MnO}_2$  was investigated by XPS to help understand its catalytic performance. The asymmetric peak located at 642.3 eV (Fig. 3(a)) indicated the existence of Mn(IV) [37], which was in good accordance with the XRD result. There were various surface O species since the O 1s spectrum could be deconvoluted into three peaks [37,38]: at 529.8–530.1 eV ( $\text{O}_\text{I}$ ) assigned to lattice oxygen, 531.3 eV ( $\text{O}_\text{II}$ ) assigned to surface adsorbed oxygen, OH groups and oxygen vacancies, and 533.0 eV ( $\text{O}_\text{III}$ ) associated with adsorbed molecular water (Fig. 3(b)). The OH groups and oxygen vacancies were the most important species for catalytic oxidation because of their high mobility and excellent activity of oxygen. From the data in Table 2, we observed that 15.7% of surface oxygen was  $\text{O}_\text{II}$  species, indicating a high catalytic per-

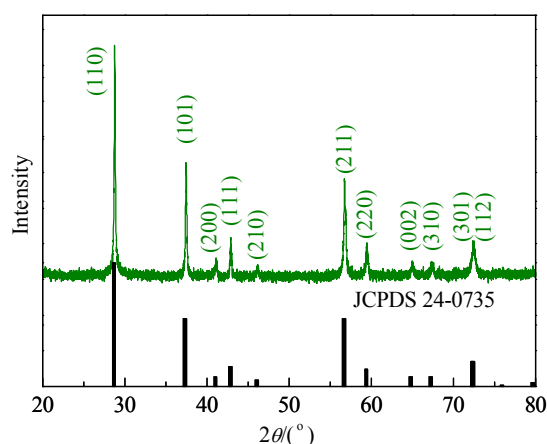


Fig. 1. XRD pattern of the  $\text{MnO}_2$  catalyst.

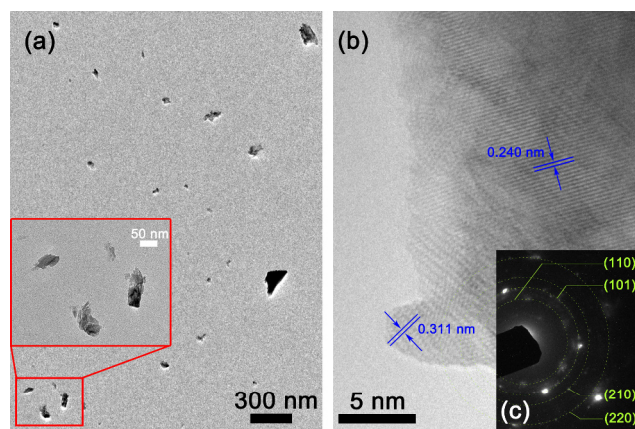


Fig. 2. TEM (a), HRTEM images (b), and selected area electron diffraction pattern (c) of the  $\text{MnO}_2$  catalyst. The inset in (a) exhibits the morphology of the  $\text{MnO}_2$  catalyst.

formance in the following experiments.

### 3.2. Catalytic oxidation of heavy oil

The oxidation and catalytic oxidation performance of the heavy oil were evaluated by TGA. The TG curves in Fig. 4 exhibited that the oxidation of heavy oil involved three stages: low temperature oxidation (50–300 °C), plateau section (300–350 °C), and high temperature (350–500 °C) oxidation.

At low temperature, partial oxidation of oil components was

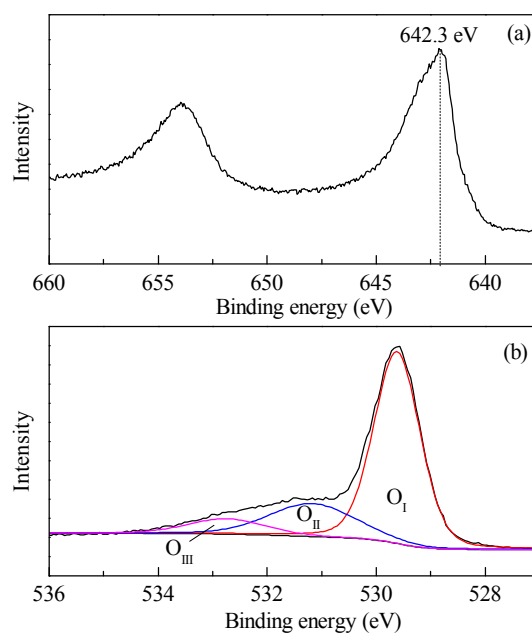


Fig. 3. Mn 2p (a) and O 1s (b) XPS spectra of the  $\text{MnO}_2$  catalyst.

Table 2  
XPS results for the  $\text{MnO}_2$  catalyst.

O species	BE (FFWHM) (eV)	At. (%)
$\text{O}_\text{III}$	532.5 (1.1)	10.0
$\text{O}_\text{II}$	531.2 (1.1)	15.7
$\text{O}_\text{I}$	529.5 (1.1)	74.2

dominant and the weight loss rate was smooth. Oxidative addition reactions are believed to dominate the reactions because a large amount of data from both laboratory and field trials revealed a significant viscosity increase of the oil produced after the low temperature period. However, in this case, since the oil was devolatilized at 300 °C before the test, a significant weight loss was observed in the temperature interval from 200 to 350 °C (Fig. 4(a)) indicating the occurrence of oxidative decomposition reactions. Both oxidative addition and cracking reactions occurred at low temperature, and each was dominant in a different temperature interval. At temperatures less than 200 °C, oxidative addition was the dominant reaction leading to little weight loss, while at 200–350 °C, oxidative decomposition became the dominant reaction resulting in a large weight loss. This indicated the possibility for the decrease of fuel deposition at the end of low temperature period using oxidative decomposition promoted by  $\text{MnO}_2$  additives. The TG profile of catalytic oxidation by the  $\text{MnO}_2$  particles displayed a larger weight loss. Total weight loss of the oil sample with  $\text{MnO}_2$  at 350 °C was increased to 26.5%, almost twice that of the oil without the catalyst (14.3%). Despite its increase in weight loss, the amount of released heat at low temperature was also enhanced. In Fig. 4(b), the peak heat flow exhibited an increase of 17.6% from 1.7 W/g to 2.0 W/g. Figure 4 demonstrated that the  $\text{MnO}_2$  catalyst facilitated the oxidative decomposition of heavy compounds and gave a promotion in heat generation at low temperature (< 300 °C). However, further evaluation of its catalytic effect on the high temperature exothermic behavior was still

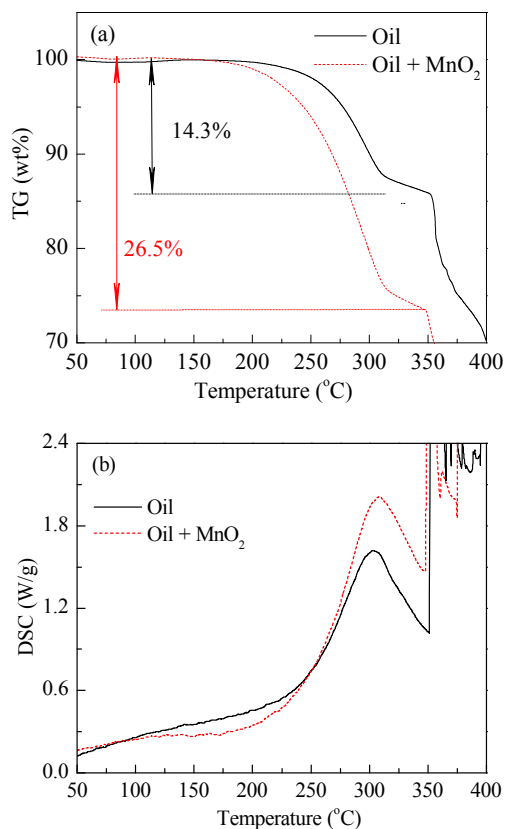


Fig. 4. TG (a) and DSC (b) of heavy oil oxidation with and without the  $\text{MnO}_2$  catalyst at low temperature.

necessary since the high temperature combustion contributes most of heat required for the *in situ* combustion.

Figure 5 illustrated the weight loss and heat release from oil oxidation in the high temperature range. The TG curves exhibited an extremely sharp weight loss as the main reactions shifted to combustion, and the end temperature was lowered because of the faster reaction rate and less residue from the low temperature oxidation. In comparison, the amount of heat released from high temperature combustion (Fig. 5 and Table 3) did not decrease despite less fuel deposition, indicating an enhancement of combustion heat by  $\text{MnO}_2$ .

The TG and DSC profiles illustrated that  $\text{MnO}_2$  decreased the amount of fuel deposition in the low temperature range, and gave the same heat from the combustion of less fuel in the high temperature range. Thus, the use of  $\text{MnO}_2$  is expected to reduce the deposition of excessive fuel in heavy reservoirs and will make *in situ* combustion more feasible.

### 3.3. Mass spectrometric (MS) analysis of oil oxidation product

The products of oil oxidation were sent to a mass spectrometer to track the catalytic oxidation of heavy oil. Inorganic products from complete oxidation ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ) and organic small molecules ( $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ) were selected as representative products. The comparison of the product flow between oil oxidation without and with  $\text{MnO}_2$  is presented in Fig. 6. The figures showed an increase in product both from complete oxidation and oxidative cracking at low temperature with the addition of

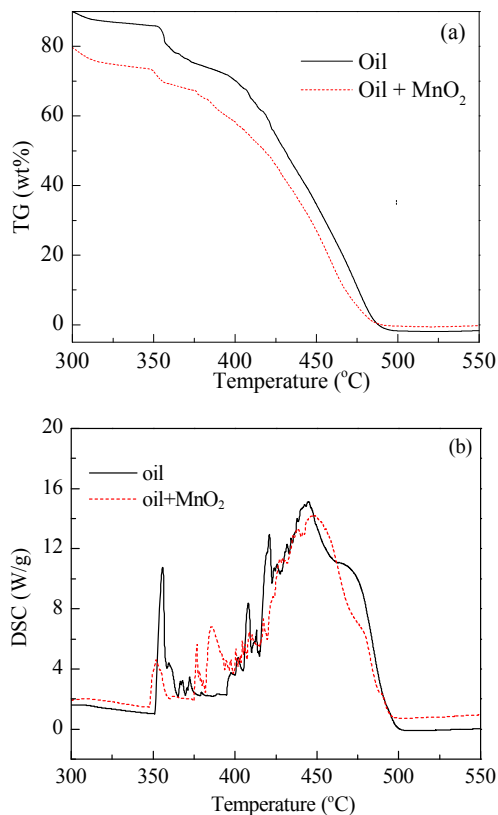


Fig. 5. TG (a) and DSC (b) of heavy oil oxidation with and without the  $\text{MnO}_2$  catalyst at high temperature.

**Table 3**TG and DSC results of heavy oil oxidation with and without the  $\text{MnO}_2$  catalyst.

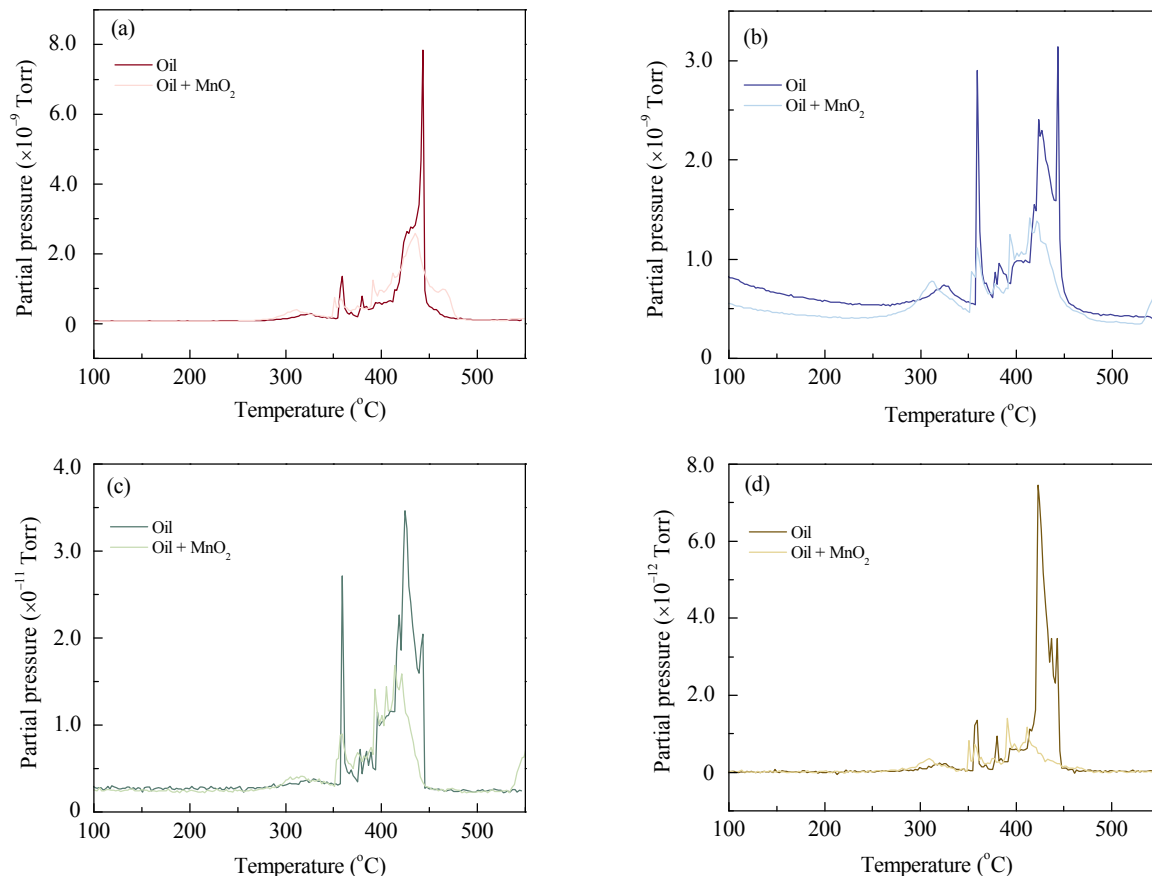
Sample	Total heat gen. (J/g)	Low temperature (50–300 °C)			High temperature (350–550 °C)		
		Weight loss (%)	Heat gen. (J/g)	Heat ratio (%)	Weight loss (%)	Heat gen. (J/g)	Heat ratio (%)
Oil	1262.4	14.3	198.3	15.7	85.7	1064.1	84.3
Oil+ $\text{MnO}_2$	1219.5	26.5	220.2	18.1	73.5	999.3	81.9

$\text{MnO}_2$ , in accordance with the promotion effect on low temperature weight loss. Compared with the doubled weight loss in the low temperature range, the observed small increase of the four products indicated the formation of other gaseous products. This would probably lead to an improvement in recovery efficiency. The catalytic effects of  $\text{MnO}_2$  on the four products in the high temperature range were prominent (Fig. 6). Since the experiments were carried out with excessive  $\text{O}_2$  flow, the detection of products from incomplete oxidation at high temperature indicated that oil combustion was a diffusion controlled process and excess  $\text{O}_2$  does not always lead to complete combustion of the oil. The concentrations of  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ , and  $\text{H}_2\text{O}$  were observed to be significant decreased, while the production of  $\text{CO}_2$  averaged over the entire high temperature range gave a cumulative amount that revealed no obvious change. Considering that there was less fuel deposited for combustion, it was the nearly constant amount of  $\text{CO}_2$  that explained why there was no change in heat generation at high temperature compared with the experiment without the catalyst. These re-

sults confirmed the promotion in the oxidation degree of the product. On the basis of the MS data, it was speculated that  $\text{MnO}_2$  facilitated the oxidative decomposition of heavy components at low reaction temperatures, accelerated the transfer rate of oxygen in the oil phase, and boosted the complete oxidation of oil components at high temperatures, which consequently led to the promotion of low temperature cracking and high temperature oxidation heat.

### 3.4. The DAEM kinetic of catalytic oxidation

The distributed activation energy method (DAEM) was employed as the kinetic analysis to provide more insight into the catalytic mechanism. The DAEM method, which is widely used in the kinetic analysis of systems with complex reactions, assumes that many irreversible first order parallel reactions with different rate parameters are involved in the system and only one reaction occurs at a specified temperature. Therefore, the overall rate  $dV/dt$  is approximated by the rate of the  $j$ -th reac-



**Fig. 6.** Mass spectra of molecular fragment ions at  $m/z = 44$  ( $\text{CO}_2$ ) (a),  $m/z = 18$  ( $\text{H}_2\text{O}$ ) (b),  $m/z = 15$  ( $\text{CH}_4$ ) (c),  $m/z = 43$  ( $\text{C}_3\text{H}_8$ ) (d).

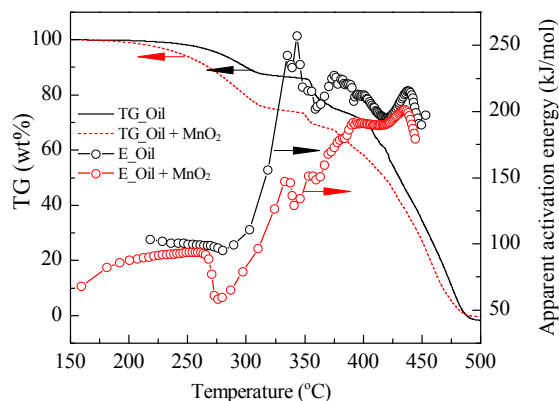


Fig. 7. Apparent activation energy of oxidation from the DAEM method.

tion at the temperature at which only the  $j$ -th reaction is occurring. The mathematical equation is given by

$$dV/dt \cong d(\Delta V)/dt = k_0 e^{-E/(RT)} (\Delta V^* - \Delta V) \quad (1)$$

where  $V$  is the total volatile evolved by time  $t$ ,  $V^*$  is total volatiles of the sample,  $f(E)$  is a distribution curve of the activation energies representing the differences in the activation energies of many first order irreversible reactions, and  $k_0$  is the frequency factor corresponding to the  $E$  value.

After mathematical transformation, Eq. (1) can be rewritten as,

$$\ln(\beta/T^2) = \ln(k_0 R/E) - \ln[-\ln(1 - \Delta V/\Delta V^*)] - E/(RT) \quad (2)$$

where  $\beta$  is the heating rate. Thus, the  $E$  and  $k_0$  value corresponding to the  $V/V^*$  value is determined by the Arrhenius plot of  $\ln(\beta/T^2)$  vs.  $1/T$  at the same  $V/V^*$  value. The activation energy of heavy oil oxidation with  $\text{MnO}_2$  catalyst was calculated by a method similar to that reported in previous publications [39–42].

The activation energy versus temperature relationship in the whole temperature range is illustrated in Fig. 7. The symbols on the profiles of the activation energy stand for the percent of weight loss from 1% to 100% with an interval of 1%. Similarly to the TG profiles, the two profiles showed similar tendency and were divided into three regions: low temperature region, transition region, and high temperature region. The activation energy was less than 150 kJ/mol in the low temper-

ature interval and 200 kJ/mol in the high temperature interval. With the addition of the  $\beta\text{-MnO}_2$  catalyst, the apparent activation energy decreased by 10–30 kJ/mol at low temperature and by 20–40 kJ/mol at high temperature. Since the apparent activation energy is defined as the minimum energy required for atoms or molecules to undergo chemical transformation, the decrease of activation energy was attributed to the reduction of the potential barrier and increase in oxygen transfer coefficient from the contribution of mobile oxygen vacancies on the surface of  $\text{MnO}_2$ . The oil mixed with  $\text{MnO}_2$  exhibited an earlier weight loss and the limits of the transition region were also shifted to higher conversion. This indicated that more reactants were involved in the low temperature oxidation and more light products were available, which was consistent with the result of the TG experiment.

#### 4. Conclusions

A  $\beta\text{-MnO}_2$  nanoparticle catalyst with rough polycrystalline edges and abundant absorbed oxygen and oxygen vacancies was used for *in situ* combustion to enhance the low temperature decomposition of heavy oil components and to promote heat release at high temperature. TGA experiments demonstrated that the total weight loss at low temperature was almost doubled from 14.3% to 26.5% by the addition of the  $\beta\text{-MnO}_2$  catalyst, and the heat release from high temperature combustion did not decline despite less fuel deposition.  $\text{MnO}_2$  promoted the low temperature cracking and the high temperature oxidative decomposition of heavy components and the increase in the transfer rate of oxygen in the oil phase. The apparent activation energies obtained by the DAEM method were decreased, which confirmed the catalytic role of the  $\text{MnO}_2$  catalyst. The outstanding performance of oil oxidation with the addition of the  $\text{MnO}_2$  catalyst would expand the applications of thermal recovery strategies and afford improved produced oil with increased oil recovery efficiency.

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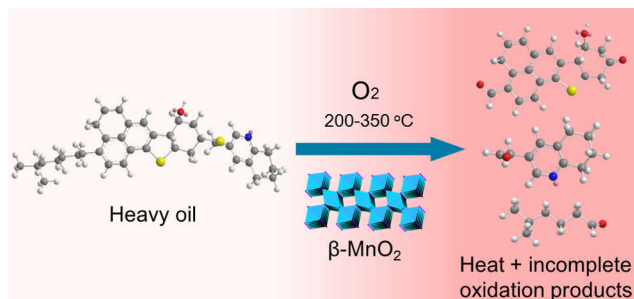
#### Graphical Abstract

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##### Controllable oxidation for oil recovery: Low temperature oxidative decomposition of heavy oil on $\text{MnO}_2$ catalyst

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$\text{MnO}_2$  nanoparticles were employed to facilitate the cracking of heavy compounds, promote heat production, and improve recovery efficiency.



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