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Viscosity Reduction and Mechanism of Aquathermolysis of Heavy Oil Co-Catalyzed by Bentonite and Transition Metal Complexes

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Abstract: At present, the research on aquathermolysis catalysts mainly focuses on the catalytic effect of external catalysts on the reaction, ignoring the fact that external catalysts will form complexes with in situ inorganic minerals after entering the reservoir. In this paper, we investigated the effects of transition metal complexes as external catalysts and bentonite as in situ catalysts on aquathermolysis, respectively. Meanwhile, the aquathermolysis reaction co-catalyzed by external and in situ catalysts was further investigated. The results show that the transition metal complexes exhibited good co-catalysis with bentonite. The viscosity reduction rate can reach 73.47% at 200 °C and 4 h with 0.1 wt.% of catalyst (NAD–Zn) addition. The addition of ethanol under the same reaction conditions will further increase the viscosity reduction rate to 84.59%. The results of thermogravimetric analysis, component analysis and boiling range analysis of heavy oil show that the heavy components in heavy oil are cracked into light components after the aquathermolysis. The results of elemental analysis show that the heteroatoms in the heavy oil were removed and the quality of the crude oil was improved. The results of GC–MS analysis of the model compounds showed that the process of aquathermolysis was mainly through the cleavage of C–C, C–N and C–S bonds to crack the macromolecules into small molecules, and then achieve the effect of viscosity reduction. The main mechanism of catalyst action is the acidic center on the surface of the bentonite and the coordination bonds formed by the transition metal complexes with the heteroatoms.

Keywords: heavy oil; catalytic aquathermolysis; viscosity reduction; co-catalyst; ethanol; mechanism

1. Introduction

With the declining extraction of light crude oil and the huge demand for crude oil for national development, people are gradually turning attention to the rich reserves of heavy oil. The biggest difference between heavy oil and conventional crude oil is its high viscosity, which poses a great challenge for extraction and transportation [1,2]. Numerous heavy oil extraction technologies have been developed to solve the problems associated with the high viscosity of heavy oil. The current methods of extracting heavy oil include hot, cold and composite extraction [3]. Thermal recovery techniques are mainly based on the sensitivity of heavy oil viscosity to temperature changes but they require the use of large amounts of heat, which is accompanied by significant energy consumption and also increases the water content in the crude oil [4]. Cold recovery techniques are mainly used to reduce viscosity by adding chemicals to the reservoir, thus changing the structure of the heavy oil material, but there are problems with con-
tamination of the formation and the oil. The combination of these two technologies will result in much higher recovery rates but with the attendant high costs [5]. Aquathermolysis technology refers to the irreversible viscosity reduction of heavy oil through the reaction between heavy oil and steam under the condition of steam injection [6,7]. Hyen pioneered the concept of aquathermolysis in the 1980s and discovered the catalytic effect of metal salts on the reaction. It is found that transition metals have obvious catalytic effect on the aquathermolysis of heavy oil [8]. Chen et al. developed a cobalt salt catalyst, and the viscosity reduction rate of heavy oil could still reach 84.5% at a catalyst addition of 0.5% and a reaction temperature of 180 °C [9]. Wang et al. synthesized a series of transition metal naphthenates (cobalt naphthenate, iron naphthenate, nickel naphthenate) as oil-soluble dispersion catalysts and achieved good catalytic results [10]. A series of studies have found that transition metal ions have obvious catalytic effect on aquathermolysis.

At present, the research on aquathermolysis catalysts has mainly focused on the development of various types of catalysts, while ignoring the fact that the catalysts will interact with the clay minerals in the reservoir to form a complex after entering the reservoir and then exert catalytic effects [11,12]. The clay minerals in the reservoir are equally catalytic to the aquathermolysis. Belgrave et al. found that reservoir minerals play an important role in the production of CO2 and H2S during aquathermolysis [13]. Monin et al. found that after aquathermolysis reaction of heavy oil in the presence of reservoir minerals a large amount of light hydrocarbon gas can be produced, the resins and asphaltene content is reduced and the viscosity of heavy oil decreases significantly [14]. Fan et al. have experimentally demonstrated that reservoir minerals can reduce the viscosity of Liaohe heavy oil by more than 23% in the presence of steam [15]. Zhang et al. found that different types of clay minerals are equally catalytic to aquathermolysis reactions [16]. Xiao et al. found that clay minerals can be used as catalysts for catalytic cracking reactions [17]. Zu et al. found that minerals have a certain catalytic capacity for the formation of gaseous hydrocarbons from organic matter [18]. In summary, clay minerals have a catalytic effect on both aquathermolysis reactions and organic matter oil formation [19,20].

When the catalyst enters the formation, it first comes into contact with clay minerals in the reservoir. Sitnov et al. found that iron oxide nanoparticles could improve the catalytic efficiency of hydrothermal pyrolysis of reservoir rock minerals [21]. As the bentonite surface is rich in hydroxyl groups, the exogenous catalyst will first adsorb with the bentonite to form a complex when it enters the reservoir [22]. This results in the in-consistency between laboratory research and field application of catalysts. Xiao Jinkai found that bentonite minerals not only have catalytic effect on catalytic cracking reaction, but also can be used as a carrier for catalysts. Clay minerals have large specific surface area, good ion exchange capacity and rich pore structure [23]. Therefore, when the exogenous catalyst enters the reservoir it will first combine with the clay in the reservoir to catalyze synergistically [24,25].

In this paper, a series of transition metal complexes (D–M) was synthesized using bipyridine and transition metal ions. At the same time, sodium bentonite (NA) was selected as the in situ catalyst, and the catalytic effects of the in situ catalyst, the exogenous catalyst and the compound formed by them on aquathermolysis were investigated. The compound formed by the interaction of internal and external catalysts and exogenous catalysts is named as NAD–M. The NAD–M were characterized by IR, TGA, and XRD, and the heavy oil were also characterized by elemental analysis, thermogravimetric analysis and SARA (S: saturates, A: aromatics, R: resins, A: asphaltenes) analysis. Several model compounds were selected to simulate the chemical component changes in the heavy oil, and the resulting products were analyzed by GC–MS. Based on these results, a reasonable speculative investigation of the reaction mechanism was carried out.
2. Results and Discussion

2.1. The Influence of Different Conditions on the Aquathermolysis

2.1.1. Effect of Catalysts on Aquathermolysis

The viscosity reduction effect of the seven complex catalysts synthesized for aquathermolysis of heavy oil is shown in Figure 1. All seven catalysts show good catalytic effects with the dosage of 0.1 wt.%, and the viscosity of the crude oil was significantly reduced after the reaction. Of the seven complex catalysts, NAD–Zn had the best catalytic effect, achieving a viscosity reduction of 73.47% at 30 °C compared to the blank group. The external catalyst (D–Zn) and in situ catalyst (NA) showed a good co-catalysis effect. Therefore, NAD–Zn was chosen for subsequent experiments [26].

![Figure 1. Effect of catalysts on the viscosity of catalytic aquathermolysis heavy oil.](image)

2.1.2. Evaluation of the Catalytic Effect of NA and D–Zn Separately

The effects of NA, D–Zn and NAD–Zn on the catalytic performance of aquathermolysis are shown in Figure 2.
Figure 2. Effect of transition metal complexes and bentonite alone on aquathermolysis.

The viscosity reduction rate was only 60.70% when the D–Zn was used as the catalyst. In situ catalyst (NA) also has a certain catalytic effect; compared with the blank group, the viscosity reduction rate is 55.10%. Compared with NA and D–Zn alone, NAD–Zn shows higher catalytic effect. Under the catalysis of NAD–Zn, the viscosity of heavy oil decreases from 392,000 to 104,000 mPa·s, and the viscosity reduction rate reaches 73.47%. Exogenous catalyst (D–Zn) and in situ catalyst (NA) show obvious synergistic catalytic effect in this research. Therefore, we selected NAD–Zn as the catalyst in the subsequent experiment.

2.1.3. Effect of Ethanol on Aquathermolysis

The effect of ethanol on the aquathermolysis reaction is shown in Figure 3. Ethanol as an auxiliary showed good facilitation of aquathermolysis reaction. The viscosity reduction of thick oil was increased from 73.47 to 84.59% by adding 10 wt.% ethanol in the presence of catalyst (NAD–Zn). The reactive hydrogen produced by ethanol during aquathermolysis can inhibit the polymerization between the small molecule radicals generated by the cracking [27].
2.2. Characterization of Heavy Oil

2.2.1. Group Composition and Elemental Analysis

The component analysis and elemental analysis of the crude oil before and after the aquathermolysis reaction are shown in Table 1 and Table 2. After the aquathermolysis reaction is completed, the saturated and aromatic hydrocarbon fractions contained in the heavy oil increase, and the asphaltene and resins fractions decrease in content. This suggests that the reactions that occur during aquathermolysis of heavy oil take place mainly between colloidal asphaltene macromolecules. As can be seen from Table 2, after the aquathermolysis reaction the elemental N and S contents of the oil samples were significantly reduced, and ethanol, as an auxiliary, further reduced their contents [28,29]. The increase in the H/C ratio in the oil samples indicates that the crude oil has been upgraded by the reformulation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturated HC, %</th>
<th>Aromatic HC, %</th>
<th>Resin, %</th>
<th>Asphaltene, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before reaction</td>
<td>32.53</td>
<td>26.68</td>
<td>18.15</td>
<td>22.64</td>
</tr>
<tr>
<td>NAD–Zn</td>
<td>33.71</td>
<td>27.96</td>
<td>16.87</td>
<td>21.46</td>
</tr>
<tr>
<td>NAD–Zn + ethanol</td>
<td>35.28</td>
<td>29.23</td>
<td>15.17</td>
<td>20.32</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>C/%</th>
<th>H/%</th>
<th>N/%</th>
<th>S/%</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before reaction</td>
<td>86.26</td>
<td>9.90</td>
<td>0.91</td>
<td>0.53</td>
<td>0.1148</td>
</tr>
<tr>
<td>NAD–Zn</td>
<td>85.91</td>
<td>10.15</td>
<td>0.82</td>
<td>0.43</td>
<td>0.1181</td>
</tr>
<tr>
<td>NAD–Zn + ethanol</td>
<td>84.97</td>
<td>10.34</td>
<td>0.76</td>
<td>0.41</td>
<td>0.1217</td>
</tr>
</tbody>
</table>

2.2.2. Wax Crystal Morphology

After the aquathermolysis reaction of the crude oil, the wax crystals in their saturated hydrocarbon fraction were observed microscopically, and the results are shown in
Figure 4. After aquathermolysis, the wax crystal morphology changes from the original aggregated and stacked mesh structure to a relatively sparse structure. The number of paraffin crystals decreases, and the degree of dispersion increases. The aquathermolysis of large molecules such as asphaltenes in heavy oil produces branched alkanes and small cyclic alkanes that dissolve some of the wax crystals, thereby increasing the fluidity of the crude oil [30].

Figure 4. Photography of paraffin crystal in saturated HC of the heavy oil before (a) and after (b) aquathermolysis.

2.2.3. Thermogravimetric Analysis of Heavy Oil

The TG curves of the heavy oil before and after the reaction are shown in Figure 5. The mass loss increased from 4.69 to 7.06% in the range of 30–150 °C. The mass of residue above 520 °C was correspondingly reduced from 10.95 to 9.21%. These results indicate that during aquathermolysis, the resin and asphaltene fractions in the heavy oil are cracked to produce saturated and aromatic hydrocarbons under the action of the cata-
After the aquathermolysis, not only is the viscosity of crude oil reduced, but the quality of crude oil is also improved.

![Graph showing mass fraction vs. temperature for before and after aquathermolysis](image)

**Figure 5.** The TG curves of heavy oil before (a) and after (b) aquathermolysis.

### 2.2.4. Distribution of Distillation Ranges

The boiling range of the oil samples after the aquathermolysis reaction is shown in Table 3. The oil sample contains more fractions with a distillation range over 350 °C, which is typical of heavy oil. When the reaction was completed, the content of the heavy oil fraction above 350 °C decreased from 66.90 to 59.89%, and the light fraction and middle fraction were increased to different degrees. This also indicates that the aquathermolysis reaction is the cracking of the heavy component of the heavy oil into the light component.
Table 3. Boiling range of heavy oil before and after the aquathermolysis.

<table>
<thead>
<tr>
<th>Boiling Range/°C</th>
<th>Blank</th>
<th>NAD–Zn</th>
<th>NAD–Zn + Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cut</td>
<td>Cumulative</td>
<td>Cut</td>
</tr>
<tr>
<td>initial boiling point</td>
<td>3.22</td>
<td>3.22</td>
<td>6.69</td>
</tr>
<tr>
<td>100–150</td>
<td>2.06</td>
<td>5.28</td>
<td>1.82</td>
</tr>
<tr>
<td>150–200</td>
<td>2.42</td>
<td>7.70</td>
<td>1.90</td>
</tr>
<tr>
<td>200–250</td>
<td>4.29</td>
<td>11.99</td>
<td>3.82</td>
</tr>
<tr>
<td>300–350</td>
<td>13.52</td>
<td>33.13</td>
<td>14.07</td>
</tr>
<tr>
<td>&gt;350</td>
<td>66.90</td>
<td>100</td>
<td>64.60</td>
</tr>
</tbody>
</table>

2.3. Characterization of the Catalyst

2.3.1. IR Characterization and Thermogravimetric Analysis of the NAD–Zn

The catalyst (NAD–Zn) was characterized by IR using NA as a blank control group, and the experimental results are shown in Figure 6a. The basic skeleton of the NA and NAD–Zn IR spectra are essentially the same. The peak at 1491.6 cm\(^{-1}\) is the C=N stretching vibration peak on the ligand dipyridyl skeleton. The peak at 1474.1 cm\(^{-1}\) is the C=C stretching vibration peak on the pyridine ring in the ligand dipyridyl. The peak at 1443.9 cm\(^{-1}\) is the stretching vibration peak on the ligand pyridine ring skeleton, and the peak at 732.9 cm\(^{-1}\) is the bending peak outside the C–H plane of the pyridine ring. This indicates that NA successfully formed a composite catalyst (NAD–Zn) with D–Zn [31].

![Graph showing IR spectra comparison between NA and NAD-Zn](image-url)
The TG curve of the NAD–Zn is shown in Figure 6b. Comparison with the NA revealed that the rate of mass change of the NAD–Zn was significantly higher than NA during the temperature rise from 110 to 650 °C. At this temperature range, the main weight loss of the NA is mainly due to the removal of adsorbed water between the bentonite layers and the dehydroxylation reaction. The main reason for the loss of weight of the NAD–Zn is that the transition metal complexes entering between the bentonite layers are unstable and decompose [32].

2.3.2. The SEM of NAD–Zn

The SEM of the catalyst (NAD–Zn) is shown in Figure 7. Compared with NA, the surface of catalyst NAD–Zn was found to be flaky. The specific surface area of the catalyst NAD–Zn was significantly increased. The change in the size of the catalyst further increases its contact area with the heavy oil and improves the catalytic effect.
2.3.3. The XRD of NAD–Zn

The XRD spectrum of NAD–Zn is shown in Figure 8. In the XRD spectrum of NAD–Zn, the (001) crystal plane diffraction peak is significantly migrated. The interlayer spacing of the catalyst was calculated by the Bragg equation ($2d\sin\theta = n\lambda$) to be significantly larger than sodium bentonite. This indicates that the transition metal complexes have successfully exchanged ions with the exchangeable Na⁺ in the sodium bentonite. The complexes have successfully entered the interlayer of the bentonite and increased the interlayer spacing of the sodium bentonite [33].

![Figure 7. The SEM of NA (a) and NAD–Zn (b).](image)

![Figure 8. The XRD spectrum of NAD–Zn.](image)
2.4. Mechanism of Aquathermolysis

2.4.1. Selection of Model Compounds

Figure 9 shows a common type of asphaltene molecular model. In the previous section, it was demonstrated that the aquathermolysis of heavy oil occurs mainly in the asphaltene. Asphaltene molecules are complex in composition and contain a large number of functional groups. Model compounds containing the same functional groups as the asphaltene molecule were selected to investigate the reaction mechanism. The model compounds selected were phenol, pyridine, thiophene, benzothiophene, quinoline, and nonylphenol.

![Figure 9: Selection of model compounds.](image)

2.4.2. The Role of High-Temperature Water

The chemical properties of water become very active at high temperatures. The dielectric constant of water drops sharply with increasing temperature, and water can dissolve more organic matter in a hot environment. As the temperature increases, the ion-product constant of water decreases significantly, which indicates that water ionizes to form more H+ and OH− and that the acid-base catalysis of water is enhanced. At the same time, the water can undergo water-gas conversion reactions, providing the necessary active hydrogen for aquathermolysis reactions [34].

2.4.3. GC-MS of Model Compounds after Aquathermolysis

After aquathermolysis reaction of phenol and pyridine, no new products were found by GC-MS analysis. The following study focuses on the reaction mechanism of aquathermolysis of thiophene, nonylphenol, quinoline and benzothiophene.

2.4.4. The Reaction Mechanism of Thiophene

The GC curves for the different reaction conditions of thiophene are shown in Figure 10. No significant new material was found to be formed on the GC curve. However, the proportion of thiophene in the reaction system decreased, presumably due to a decomposition reaction of thiophene to gaseous low-carbon hydrocarbons, and therefore no products were found to be formed in the liquid phase products. A diagram of the aquathermolysis mechanism of thiophene is shown in Figure 11. During the aquathermolysis of thiophene, the H+ dissociated from the water under high temperature conditions attacks on the sulfur atoms, causing them to protonate. Thiophene opens its ring for the first hydrolysis to produce intermediates such as thiols and enols, which undergo isomerization to form aldehydes. The aldehyde is unstable and undergoes secondary hydrolysis to produce CO, H2S and low-carbon hydrocarbons [35].
Figure 10. GC curves of thiophene under different reaction conditions.

Figure 11. Diagram of the aquathermolysis reaction mechanism of thiophene.

2.4.5. The Reaction Mechanism of Nonylphenol

The GC curves of nonylphenol under different reaction conditions are shown in Figure 12. The reaction mechanism diagram for nonylphenol is shown in Figure 13. The aquathermolysis reaction of nonylphenol resulted in the formation of a variety of substances. The analysis revealed that the aquathermolysis of nonylphenol resulted in the breakage of the C–C bond and the formation of octylphenol, pentylphenol and butylphenol [36]. Breakage of chemical bonds at different locations may have occurred in
nonylphenols, and there may have been interactions of the resulting active chains to re-create new macromolecules.

**Figure 12.** GC curves of nonylphenol under different reaction conditions.

**Figure 13.** Diagram of the aquathermolysis reaction mechanism of nonylphenol.
2.4.6. The Reaction Mechanism of Quinoline

The GC curves of quinoline under different aquathermolysis conditions are shown in Figure 14. The quinoline underwent a decomposition reaction in the presence of ethanol, and the product of the reaction was detected as ethylbenzene. The mechanism of the aquathermolysis reaction of quinoline is shown in Figure 15. The quinoline is first reduced to 1,2,3,4-tetrahydroquinoline by a alkylation reaction. This is followed by a ring-opening reaction to form 3-phenyl-1-propylamine, which under high temperature and pressure results in the breakage of the carbon chain, eventually producing ethylbenzene and ammonia. The presence of ethanol provides sufficient active hydrogen in the reaction system to ensure that the hydrogenation and decomposition reactions take place [37].

![GC curves of quinoline under different conditions](image_url)

*Figure 14. GC curves of quinoline under different reaction conditions.*
Figure 15. Aquathermolysis reaction mechanism of quinoline.

2.4.7. The Reaction Mechanism of Benzothiophene

The GC curves of benzothiophene under different reaction conditions are shown in Figure 16. The product was ethylbenzene by GC-MS analysis. The mechanism of the benzothiophene reaction is shown in Figure 17. Benzothiophene first undergoes hydrogenation to form 2,3-dihydro-1-benzothiophene, followed by C-S bond breaking and ring opening to produce ethylbenzene and hydrogen sulfide [38].

Figure 16. GC curves of benzothiophene after reaction under different reaction conditions.
Figure 17. Aquathermolysis reaction mechanism of benzothiophene.

2.4.8. Mechanisms of Aquathermolysis Reactions in Heavy Oil

The main chemical changes that occur during the aquathermolysis reaction of heavy oil are shown in Figure 18. The aquathermolysis reaction of heavy oil is mainly the breaking of C–C, C–N and C–S bonds in asphaltene. The heteroatoms in the heavy oil are removed in the form of H₂S and NH₃. The reticulation of asphaltene is broken, and the viscosity of heavy oil is reduced [39]. The presence of ethanol and water provides a large amount of active hydrogen for the cleavage reaction, while inhibiting the polymerization reaction between the small active chains.

Figure 18. Chemical changes occurring in the aquathermolysis reaction of heavy oil.

2.5. The Catalytic Mechanism of NAD–Zn

The schematic diagram of the catalytic mechanism of the catalyst is shown in Figure 19. The transition metal complex central ion can provide orbitals for lone pairs of electrons on heteroatoms (N, S, O), thus forming coordination bonds. After the formation of a coordination bond, the dynamic induction effect can reduce the bond energy of C–S bond and C–N bond [40]. The B acids and L acids contained in the bentonite can promote the reaction processes, such as ring activation and intermediate structure stabilization after ring opening. At the same time, the presence of a large number of broken bonds on the surface of bentonite minerals has a strong adsorption effect on the organic macromolecules in heavy oil, which increases the contact area between heavy oil and catalyst [41].
Figure 19. Catalytic mechanism of bentonite and transition metal complexes.

3. Materials and Methods

3.1. Material

Petroleum ether, toluene, ethanol, bipyridyl and transition metal chloride salts were purchased from Xian Chemical Reagent (Xi’an, China) Co., Ltd. (AR reagent grade) and were used without further purification. Phenol, pyridine, thiophene, benzothiophene, quinolone and nonylphenol purchased from Aladdin Reagent (Shanghai, China) Co., Ltd. were all of the analytical grades. Therefore, no further purification was needed. Heavy oil L8401 used in the experiments was obtained from Henan oilfield (Henan, China). The basic physical properties of the oil samples are shown in Table 4.

Table 4. Physical properties of heavy oil.

<table>
<thead>
<tr>
<th>Pour Point /°C</th>
<th>Saturated HC, %</th>
<th>Aromatic HC, %</th>
<th>Resin, %</th>
<th>Asphaltene, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.0</td>
<td>32.53</td>
<td>22.68</td>
<td>18.15</td>
<td>22.64</td>
</tr>
</tbody>
</table>

3.2. Synthesis of the Catalysts

The seven transition metal chlorides and dipyridyl were added separately to a 100 mL flask in a molar ratio of 1:2, using ethanol as the solvent. The mixture is heated to reflux at 80 °C for 4 h. After the reflux is completed, sodium bentonite is selected as the catalyst carrier, and the required mass of sodium bentonite is added according to the minimum ion exchange capacity of sodium bentonite. Continue heating and refluxing at 80 °C for 4 h. At the end of the reaction, the mixture was washed continuously by centrifugation with ethanol until the supernatant was colourless. The product obtained by evaporation of the solvent was the catalyst. The synthesis process of the NAD–M is shown in Figure 20. The synthesis of the transition metal complexes is shown in Figure 21.
Figure 20. The synthesis process of NAD-M.

Figure 21. Synthesis of transition metal complexes.

3.3. Characterisations of Catalysts

The catalyst was characterized by (FT-IR) Fourier Transform Infrared Spectroscopy (Thermo Electron Co., Waltham, MA, USA). Wavenumber range from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\) and 64 scans were used for measurement. The TGA (Thermogravimetric Analysis) was carried out using a TGA/SDTA851 instrument (METTLER TOLEDO, Zurich, Switzerland) over the temperature range of 35–700 °C, at a heating rate of 20 °C/min. The measurements were carried out in N\(_2\) atmosphere (flow rate 16.66 cm\(^3\)/min) by using alumina crucibles. The catalyst was also characterized by scanning electron microscope (SEM, JSM-6390A, JEOL, Tokyo, Japan) and diffraction of X-rays (XRD, D8ADVANCE, Bruker, Berlin, Germany).

3.4. Experimental Conditions

Experiments were carried out by introducing predetermined mass ratios of water to heavy oil (30 wt.%), with a catalyst to crude oil mass ratio (0.1 wt.%), into the reactor. Each mixture was heated to and maintained at 200 °C for 4 h. The reactor and the mixture were cooled to about 50 °C in a water bath. The mixture was then poured into a beaker and the oil decanted for transport properties and compositional tests. When the reaction is complete, cool to room temperature and pours the mixture from the reactor into a measuring cup. The measuring cup is placed in a water bath and after the oil and water have separated, the upper oil sample is taken for viscosity measurement.
The model compounds (phenol, pyridine, thiophene, benzothiophene, nonylphenol, quinoline) were dissolved in toluene at 7 wt.% by mass. The aquathermolysis reaction was carried out under the reaction conditions described in Section 2.5. When the reaction was completed, the mixture was centrifuged at 4000 r/min for 20 min, and the supernatant was taken for GC–MS analysis. The compositional analysis of the model compounds after the reaction was carried out using GC–MS (GC-7890B/MSD-5977A, Agilent Technologies, California, USA). The carrier gas was hydrogen with a flow rate of 25 mL/min. The composition analysis of the samples was evaluated by the database of DRS compounds.

3.5. Characterization of Heavy Oil before and after Reaction

The viscosity of the treated heavy oil was determined using a BROOKFIELD DV-II+ programmable Viscometer (Brookfield, Stoughton, USA) at certain temperatures according to Industrial Standard of China Petroleum, SY/T0520-2008. The density and the pour point of the crude oil were determined according to GB/T 1884-2000 and SY/T 2541–2009, respectively. Four compound groups, namely saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltene (SARA) were separated by the column chromatography-based method according to Industrial Standard of China Petroleum SY/T 5119. The four elements C, H, N and S contained in the heavy oil before and after the reaction were analyzed as a percentage using an EL-2 elemental analyzer (Elementar, Berlin, Germany). The saturated hydrocarbon was separated from crude oil by using the method in accordance with SY/T 5119-2016. The influence of crude oil flow improver on the morphology of wax crystal was observed by a polarizing microscope (BX41, OLYMPUS, Tokyo, Japan). During each measurement, the sample was firstly kept at 50 °C to eliminate the wax crystals. Subsequently, the sample was cooled down to 15 °C within 5 min. The formation and morphology of the wax crystals were investigated. An external thermostat was used to keep the temperature at 15 °C.

4. Conclusions

In this paper, a series of transition metal complexes was synthesized as exogenous catalysts. By simulating the interaction between the exogenous catalyst and the clay minerals in the reservoir after entering the reservoir, a clay-based transition metal complex catalyst that actually works in the field was obtained. The results show that bentonite and transition metal complexes have an obvious co-catalytic effect. NAD–Zn has the highest catalytic activity, with a viscosity reduction rate of 73.47%. As a hydrogen donor, ethanol can increase the viscosity reduction rate to 84.59% with the dosage of 10 wt.%. SARA analysis, TGA analysis and wax crystal observation of the reaction oil samples showed that the viscosity reduction effect was achieved mainly through the cleavage of heavy components and removal of heteroatoms. Six model compounds were selected to investigate the mechanism of aquathermolysis reactions. Further studies have shown that the process of aquathermolysis of heavy oil mainly occurs through the breaking of C–S bonds, C–N bonds and alkyl chains. The main catalytic mechanism of NAD–Zn is the rich acidic center contained in the bentonite surface and the reduction of C–N bond, C–S bond and C–C bond energy by transition metal ions. The mechanism of bentonite and transition metal complexes co-catalyzed by hydrothermal cracking for viscosity reduction was studied. We believe that the reservoir minerals have a good synergistic catalytic effect with the artificially added exogenous catalyst, which can further reduce the viscosity of heavy oil. This work is of guiding significance to the development of new catalysts in the future.

**Author Contributions:** Data curation, methodology and formal analysis, writing, W.Z.; investigation, validation, supervision, writing—review and editing, Q.L.; formal analysis, data curation, S.P.; conceptualization, data curation, Y.L.; supervision, resources, project administration, review and
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**Conflicts of Interest:** The authors declare no conflict of interest.

**Reference**


