Research Article

Enhanced Heavy Oil Recovery in Mild Conditions by $SO_4{}^{2-}$/TiO$_2$-ZrO$_2$ Solid Superacid Prepared by Different Methods

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The important key of heavy oil efficient exploring is to decrease the viscosity and increase the flowability. Solid acid catalyst is one of the commonly used catalysts to reducing the viscosity of heavy oil, but good dispersion in oil phase and better catalytic activity are difficult to achieve. Herein, ZrO$_2$-TiO$_2$ was selected as the fundamental catalyst because of its superior solid superacid properties, and CTAB was selected as the surfactant package coat to help enhance catalytic activity. The as-prepared catalysts were characterized systematically by TEM, XRD, FTIR, and N$_2$ adsorption-desorption isotherms measurement. The reduction efficiency of the heavy oil viscosity achieved as high as 66.3% at 180°C. At the same time, the portion of asphaltenes and resins slipped down by 4.93% and 3.78%, respectively, while saturated and aromatic hydrocarbon component increased by 5.37% and 3.26%, respectively, indicating that our catalyst showed a good activity for reducing the viscosity and improving the quality of heavy crude oil.

1. Introduction

Nowadays, with the excessive development and rapid consumption of the conventional energy resources, petroleum with high quality and natural gas cannot satisfy the present demands for energy. Economic and efficient exploitation of the heavy oil and other crude oils has attracted more and more attention. The reserves of heavy crude oil all over the world are abundant, but the high viscosity and poor liquidity of heavy oil make it very difficult to extract. Therefore, the key point of extraction of the heavy oils is to decrease the viscosity and increase the liquidity [1–3].

It was first reported in 1982 by Hyne that some transition elements could behave as effective catalysts in hydrothermal cracking reaction of heavy oils. With the addition of transition elements such as Ni and Cu, the viscosity of heavy oil is reduced obviously after the hydrothermal reaction. Since then, the aquathermolysis catalytic method of heavy oil has been developed rapidly [4–6]. Following Hyne's footsteps, researchers have done a lot of work to develop effective catalysts and study the mechanism of the catalytic reduction in heavy oil. Common catalysts used for heavy oil reduction are mainly water-soluble catalysts, oil-soluble catalysts, dispersed catalysts, and acid catalysts [7]. Besides, in

the aquathermolysis process, addition of the organic solvents of toluene, naphthalene, tetrahydronaphthalene, cyclohexane, and methylcyclohexane as hydrogen donor can further improve the reaction efficiency [8].

Water-soluble catalyst is typically mineral salt containing transition metals. Previous studies of organic chemistry and catalytic theory proved that the groups which contain heteroatoms (N, O, and S) in the heavy oil could react with transition metals. Heteroatom-containing macromolecule would pyrolyze into smaller ones efficiently, leading to reduction of viscosity and decrease of density of heavy oil [4, 6]. However, it is difficult for water-soluble catalysts to disperse evenly into the organic phase during hydrothermal cracking reaction, so the practical aquathermolysis reaction could only happen in the interface between oil and water; therefore, the catalytic efficiency would be weakened to a great extent. Most of oil-soluble catalysts were organometallic compounds [9, 10], which can disperse uniformly into the oil, contacting closely with reservoir, and as a result, the catalyst would be more fully utilized. However, in practical application, large amounts of solvents carriers (e.g., gasoline and kerosene) were utilized to carry catalysts into the reservoir, which would consume vast quantities of light oil and increase the costs. Dispersed nanocatalyst has attracted much attention and has been

investigated intensively recently [11, 12], but nanoparticles easily agglomerate together and are also easily deactivated by the heteroatoms [13, 14].

Solid acid catalysts belong to Lewis acid, including solid superacid and heteropolyacid catalysts, possessing strong acidity and oxidizability [15, 16]. Numerous studies have proved that superacid exhibited good catalytic activity in many organic synthesis reactions, such as esterification and hydrocarbon chain isomerization [17–19]. And it was reported that solid superacid such as WO_3-ZrO_2 and Sn^{2+}/ZrO_2 has been used in heavy oil viscosity reduction at moderate condition ($T \leq 200°C$, $P \leq 10$ MPa), and the catalytic effect on reducing the viscosity of heavy oil was excellent [20, 21].

Based on previous studies, we know that solid superacid catalyst has many advantages comparing with the traditional catalyst, such as high catalytic efficiency, selectivity, and less adverse effect [22, 23]. The dispersion of the inorganic solid catalyst in oil phase is very important, which has a strong influence on the reaction efficiency. Appropriate amphiphilic surfactant modification is beneficial to improving the dispersion of catalyst in oil, which would further provide help to the catalytic reaction. Amphiphilic catalyst has been used to enhance the quality of heavy crude oil, and surfactant promoting the dispersion of catalyst has been reported comprehensively [24–27]. In this work, ZrO_2-TiO_2 was selected as the fundamental catalyst because of its superior solid superacid property. Then a series of SO_4^{2-}/ZrO_2-TiO_2 catalysts were prepared by different synthetic methods, and CTAB was selected as surfactant package coat to help enhance catalytic activity. The as-prepared catalysts were characterized systematically by TEM, XRD, FTIR, and N_2 adsorption-desorption isotherms measurement. The quality of crude oil sample was identified by viscosity measurement and SARA analysis.

2. Experiment Section

2.1. Preparation of the Solid Superacid Catalysts with Different Methods.
One of the preparation methods of the catalysts was impregnation method. Typically, a certain amount of $TiCl_4$ and $ZrOCl_2 \cdot 8H_2O$ was dissolved in 200 mL distilled water, and the pH of the solution was adjusted to 9~10 by $NH_3 \cdot H_2O$ solution. The oxide was formed by hydrolysis of titanium ion and zirconium ion. Zirconium hydroxide and titania were uniformly grown together to form a hybrid material. After aging for 24 h, the precipitate was filtered, washed by deionized water to neutral, and dried. After that, the powder was impregnated by H_2SO_4 solution (0.5 mol/L) for 6~10 h, then filtered, and dried at 70°C in vacuum overnight. At last, the product was calcined at 550°C for 3 h, and hydroxide dehydrated to form the crystal oxide. The catalyst obtained by this impregnation method was denoted as ZT-I. The second method for preparation of the catalyst was hydrothermal approach. The reactant reagents were similar with the aforesaid impregnation method, and the mixing solution was transferred into the 100 mL PTFE reactor, keeping 110°C for 24 h. During hydrothermal reaction, high temperature and pressure promoted the collision of hydrated zirconia colloids

via oxolation to stabilize the zirconia structure. Conditions during dipping process and calcination were identical to the impregnation method. During the subsequent calcination process, a large amount of zirconia crystal was obtained and signed as ZT-H. Furthermore, CTAB was applied as the surfactant during immersion in H_2SO_4 before calcination to prevent the nanoparticles growing up and aggregating in the sintering process. CTAB could be removed during calcination. The obtained product was marked as ZT-H-C.

In order to further improve the dispersion of the catalyst in the oil, CTAB was used as package coat. 1 g of as-prepared ZT-H-C catalyst was dispersed in 50 mL ethanol, and then a given mass of CTAB was added to form a critical micelle. The mixing solution was stirred for 10 h, and ultimately, the catalyst was separated and dried in vacuum. The obtained catalyst was signed as CTAB@ZT-H-C.

2.2. Measurement of the Properties of Heavy Oil

2.2.1. Catalytic Viscosity Reduction of Heavy Oil.
Heavy oil from Shengli Oilfield (Dongying, China) was selected as feed oil. A series of catalytic thermolysis reactions were conducted at 180°C in a 500 mL high-pressure reactor for 24 h, and the addition amount of catalyst was 1%. After the reaction, the oil was taken out when cooling down, removing the separated water. 7 mL of the oil was taken out to measure the viscosity with viscometer (Brookfield DV-III) at 50°C. The viscosity reduction yield was calculated according to $\Delta\eta = (\eta_0 - \eta)/\eta_0 \times 100\%$, in which $\Delta\eta$ refers to the viscosity reduction rate of the heavy oil after the catalytic reaction and η_0 (mPa·s) and η (mPa·s) refer to the viscosity of the feed heavy oil before and after the catalytic aquathermolysis reaction, respectively.

2.2.2. Separation of Four Group Compositions (SARA).
Component analysis of four groups in heavy crude oil samples was conducted according to test method for separation of asphalt into four fractions of NB/SH/T 0509-2010. Asphaltene was precipitated from crude oil by n-heptane and further chromatograph separation of non-asphaltic oil components (saturates, aromatics, resins, and asphaltenes) was carried out in a column filled with alumina.

2.3. Catalysts Characterization.
A transmission electron microscope (TEM), JEOL JEM-2010 with accelerating voltage 200 kV, was chosen to observe the morphology of catalysts. X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert Pro X-ray diffractometer (Holland) (Cu $K\alpha$ radiation; 2θ range 15~85°, step size 0.08°, time per step 1.0 s, accelerating voltage 40 kV, and applied current 40 mA). The Brunauer-Emmett-Teller (BET) specific surface area of the samples was determined by using N_2 adsorption-desorption method with Quadrasorb SI equipment (pretreatment: 200°C/6 h). Fourier transform infrared spectrometry (FTIR; AVATAR-360, Nigaoli Instrument Company, USA; wavenumber range: 365–3700 cm^{-1}) was used to detect the functional groups contained on the surface of catalyst.

The acidity of the catalysts was examined by Hammett indicator, and m-chloronitrobenzene ($pK_a = -12.4$) was
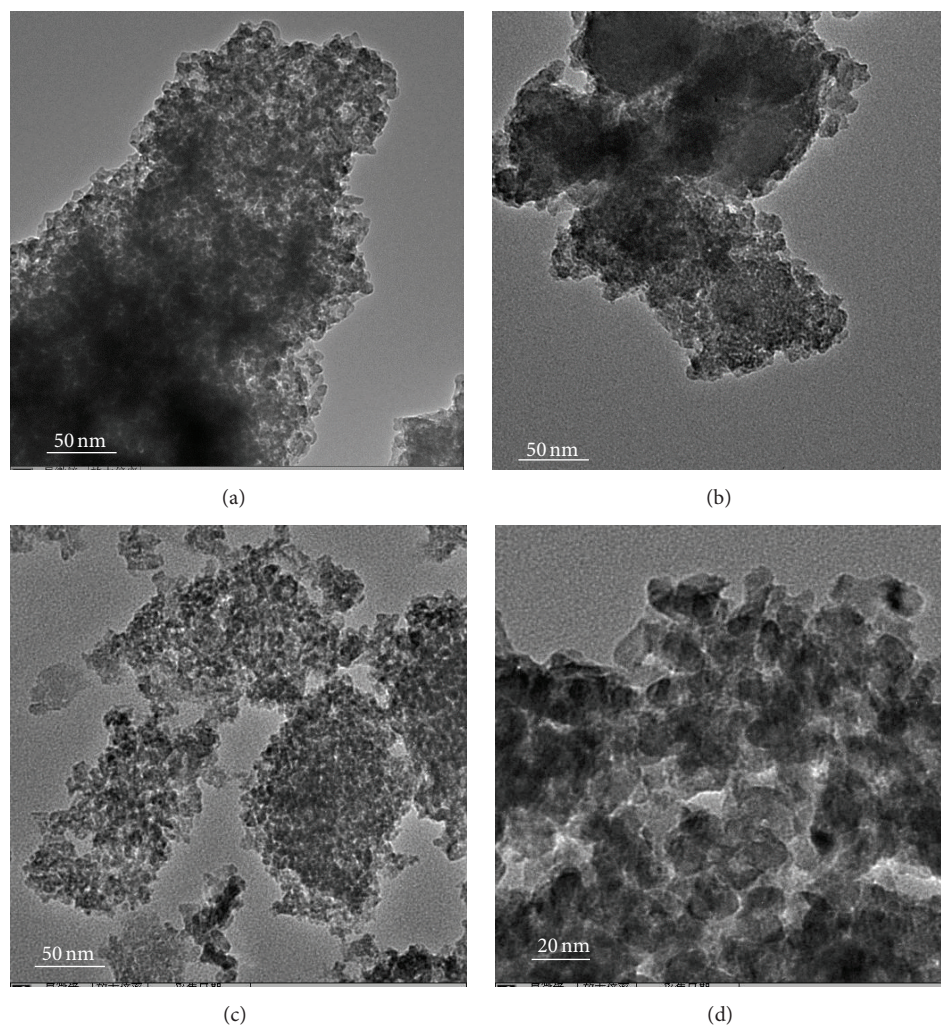
(a)

(b)

(c)

(d)

FIGURE 1: TEM of catalysts. TEM images of ZT-I (a), ZT-H (b), and ZT-H-C (c), HRTEM image of ZT-H-C (d).

chosen as the indicator. Take a small quantity of the catalyst powder into 2 mL indicator, and the color of catalyst changes from white to yellow after 30 min, implying the existence of superacid sites.

3. Results and Discussion

Generally, the different preparation methods will have a large effect on the morphology of the superacid catalyst. The different morphologies of superacid catalysts were shown in Figure 1. Observing the images of Figures 1(a) and 1(b), no apparent difference was found between ZT-I and ZT-H. Both of the particles obtained by the impregnation or hydrothermal method aggregated seriously, and the dispersion was not well. Figure 1(c) was the TEM image of ZT-H-C, and the dispersion of catalyst ZT-H-C improved, implying that when CTAB was added as a surfactant in the hydrothermal process, it had the ability to increase the dispersion of the catalyst and inhibit the crystal particles of catalyst growing up in the process of calcination treatment and further develop the pore structure. The high resolution TEM image in Figure 1(d)

clearly showed that ZT-H-C exists mainly as nanoparticles about 20 nm.

The phase structure of catalysts was analyzed by XRD technique. Figure 2 displayed the XRD patterns of ZT-I, ZT-H, and ZT-H-C superacids. The pattern of ZT-I showed that the catalyst prepared by the impregnation method was amorphous. The characteristic diffraction peaks at about 2θ = 25.4° and 30.2° in pattern of ZT-H were perfectly assigned to the (101) crystal faces of anatase TiO_2 and tetragonal ZrO_2 [28, 29]. And the tetragonal phase was dominant, which was in favor of the formation of superacid site. This indicated that impregnation process was in favor of integrated crystallinity, which further increased the acidity of catalyst and the catalytic efficiency. Comparing with pattern of ZT-H, the peak intensity of pattern ZT-H-C decreased, which was in accordance with TEM results. When CTAB was added as the surfactant, the particle size of superacids decreased, and that will lead to broadening and decrease of the diffraction peak.

The BET surface area and pore volume of a catalyst have a large effect on the efficiency of the catalytic reaction, and the large specific surface area can provide more reaction sites to

TABLE 1: Results of N_2 adsorption-desorption measurement of catalysts ZT-I, ZT-H, and ZT-H-C.

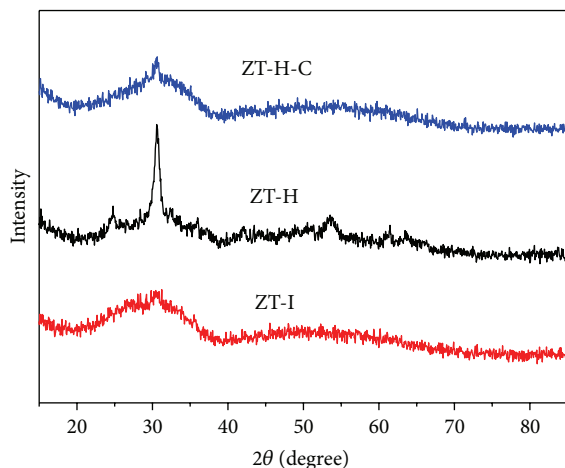| Sample	Pore radius (nm)	Total pore volume (cc/g)	P/P_0	Surface area (m^2/g)
ZT-I	2.80	0.10	0.99	72.09
ZT-H	5.38	0.06	0.99	20.16
ZT-H-C	43.20	17.44	0.99	80.74

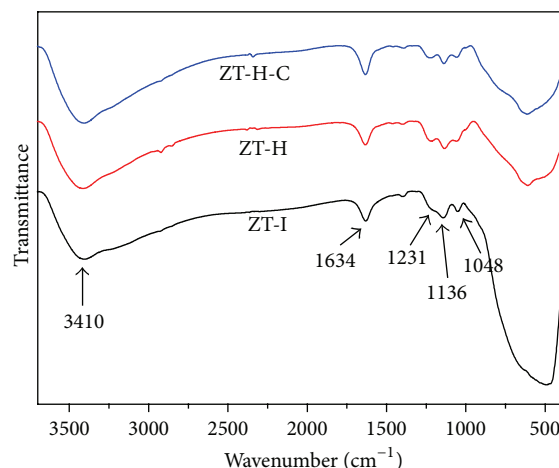FIGURE 2: XRD pattern of catalysts.

FIGURE 3: FTIR spectra of catalysts.

TABLE 2: The viscosity value and viscosity reduction rate of heavy oil after 24 h of hydrothermolysis reaction at 180°C with different catalysts.

Sample	Viscosity (mP·s)	Viscosity reduction rate
Heavy oil feed	80500	—
No catalyst	51290	36.3%
ZT-I	37500	53.4%
ZT-H	32900	59.1%
CTAB@ZT-H-C	27130	66.3%

help enhance catalytic activity. The results of N_2 adsorption-desorption measures of samples were listed in Table 1. The calculated BET specific surface areas of ZT-I, ZT-H, and ZT-H-C were 72.09, 20.16, and 80.74 $m^2 \cdot g^{-1}$, respectively. TiO_2-ZrO_2 obtained through the hydrothermal method possessed a better crystallinity, which could be deduced from the XRD results, so the BET surface area of ZT-H was the smallest. And for ZT-H-C, CTAB acted as the surfactant in the growth of the crystal and was removed in the calcination process, so BET surface area of ZT-H-C was the largest. Table 1 also illustrated that the pore radius of ZT-I, ZT-H, and ZT-H-C was 2.79, 5.37, and 43 nm, respectively. In the heterogeneous catalysis, the existence of the large pores was favorable to transport the reactants and products. Because of the larger molecules and higher viscosity of heavy oil, it is hard to utilize the small pore in the catalytic reaction. The larger pore radius of ZT-H-C may be favorable to improve the catalytic efficiency. Meanwhile, the total pore volume of ZT-H-C was as large as 17.44 cm^3/g, which would be advantageous to the catalytic reaction.

Figure 3 demonstrated the FTIR spectra of ZT-I, ZT-H, and ZT-H-C superacids. The absorption peaks at 3410 and 1634 cm^{-1} corresponded to the stretching vibration absorption of the surface adsorbed hydroxyl and nanoparticle-bound water molecules, respectively [30]. Besides, no absorption peak at 1620–1630 cm^{-1} was observed, which implied that the S=O bond in the superacid catalysts existed in bonding form other than ions absorbed on the surface. The symmetric stretching vibration peaks at 1136 cm^{-1} and 1048 cm^{-1} were assigned to O=S=O and O-S-O bonds, respectively. Furthermore, the absorption peak of SO_4^{2-} at 1231 cm^{-1} referred to bidentate chelating between SO_4^{2-} and metal oxide [31]. The absorption bands in the wavenumber regions of 1250–1010 cm^{-1} corresponded to the stretching vibration absorption of S=O, the characteristic absorption peaks of superacid, and they are attributed to the surface bidentate chelating adsorption of SO_4^{2-} and TiO_2-ZrO_2 [28, 29]. From the above analysis, we could draw the conclusion that sulfate superacid had formed on the oxide surface of the catalyst, which was consistent with the result of the Hammett indicator test, and the acidity was above −12.4.

The catalytic activities of the catalysts were evaluated by monitoring heavy oil viscosity reduction at 180°C for 24 h. As can be seen in Figure 4, without the assistance of catalysts, the viscosity reduction yield was only 36.3%. The viscosity of heavy crude feed oil decreased from 80500 mPa·s to 51290 mPa·s as presented in Table 2. This result indicated that reducing the viscosity relying on high temperature alone was unreasonable. When catalysts were introduced into the aquathermolysis reaction system, the viscosity reduction yield was enhanced on different levels. We noticed that the

TABLE 3: Results of SARA analysis between heavy oil feed and the sample after catalytic reaction.

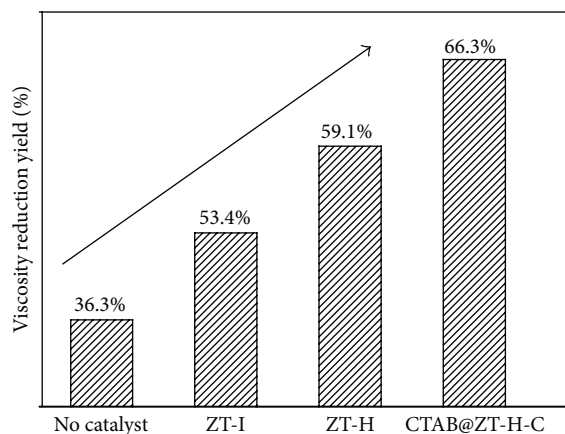| Sample	Fraction (%)				Viscosity (mPa·s)
	Saturates	Aromatics	Resins	Asphaltenes	
Heavy oil feed	29.97	24.83	35.91	9.36	80500
CTAB@ZT-H-C	35.34	28.09	32.13	4.43	27130

FIGURE 4: Viscosity reduction rate of heavy oil with catalysts.

viscosity reduction rate of heavy oil with ZT-I and ZT-H-C was 53.4% and 59.1%, respectively, and the corresponding viscosity value was 37500 mPa·s and 32900 mPa·s, respectively. Though the BET surface area of ZT-I was larger than that of ZT-H-C, the catalytic activity of the latter was still higher, indicating that the BET surface area was not the main parameter for the catalytic reaction of the heavy oil. The better crystallinity of ZT-H prepared by the hydrothermal method was beneficial to heavy oil viscosity reduction.

After CTAB was added to improve the dispersion of the catalyst in oil, the catalytic activity increased largely, the viscosity of heavy oil decreased to 27130 mPa·s, and the viscosity reduction yield reached 66.3% for CTAB@ZT-H-C. Samples with good crystallinity prepared by hydrothermal method had more strong acid sites to a certain extent, which would promote the bond breaking in the process of thermal cracking of macromolecular compounds in heavy oil [32, 33]. The increased specific surface area made acid sites react with reactants in heavy oil more adequately. Meanwhile, the sample of big hole was beneficial to mass transfer in heterogeneous catalytic process. What is more, the addition of CTAB was advantageous to the dispersion of catalyst in the oil phase, which also contributes to the catalytic reaction. In consequence, the enhanced catalytic activity of CTAB@ZT-H-C was due to the big surface area, more acid reaction sites, and better dispersion in feed oil. The heavy oil viscosity reduction increased remarkably at the existence of catalysts compared to no catalysts, showing CTAB@ZT-H-C as a promising potential application in the industrial production of heavy crude oil.

Through component analysis of four groups in heavy crude oil in Table 3, it is not difficult to find that heavy constituents decreased, while light components increased. The portion of asphaltenes decreased from 9.36% to 4.43% and that of resins decreased from 35.91% to 32.13%. What is more, the amount of saturates and aromatics increased by 5.37% and 3.26%, which was in accordance with the viscosity test results. Herein, we can safely draw the conclusion that partial big molecules in resins and asphaltenes disintegrated into relatively small fragments dissolving into saturated and aromatic hydrocarbons, leading to reducing the viscosity of heavy crude oil.

4. Conclusions

A series of solid superacid catalyst samples were synthesized through impregnation and hydrothermal methods. ZT-H-C showed excellent catalytic activity towards the aquathermolysis reaction of the extra-heavy oil of Shengli Oil Field due to its superior properties, such as big BET surface area, suitable aperture size, good crystallinity, and existence of superacid sites. Furthermore, when CTAB was added as the surfactant, the viscosity reduction efficiency achieved 66.3% on the sample of CTAB@ZT-H-C, which was the highest efficiency. At the same time, the amount of asphaltenes and resins slipped down by 4.93% and 3.78%, while saturated and aromatic hydrocarbon components increased by 5.37% and 3.26%, respectively. This result indicated that the surfactant enhanced the dispersion of the catalyst to heavy oil, and that would help the catalytic reaction more adequately.

Competing Interests

The authors declare that they have no competing interests.

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