

Preparation of phase transfer functional catalysts and their application in viscosity reduction of heavy oils

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Four kinds of nanosilica-supported metallic and metatitanic acid nanocatalysts were synthesised as potential phase transfer catalysts for enhancing heavy oil recovery *via* a liquid-reduction method. The catalysts were carried by water and transferred into oil phase, and the catalytic performance of catalysts for the aquathermolysis reaction and viscosity reduction of the extra-heavy oil recovered at Shengli Oilfield (Dongying, China) was investigated. At a mass fraction of 1%, an aquathermolysis reaction temperature of 150°C and an aquathermolysis time of 36 h, the as-synthesised silica/zero valence iron and nickel (denoted as SiO₂/Fe/Ni) catalyst was able to reduce the apparent viscosity of the two kinds of heavy oils by 79.3 and 77.6%, showing promising application in the industrial production of heavy crude oil.

1. Introduction: With the prospect of the running out of conventional hydrocarbon resource, heavy oil as the major energy with high viscosity and solidification point was increasingly drawing attention in recent years [1]. As we all know, the high viscosity of heavy crude oil was due to the existence of internal macromolecular compounds, such as asphaltene with resin, so that, breaking down larger molecules into smaller ones (saturated hydrocarbons and aromatic hydrocarbons) was necessary for reducing the viscosity of heavy crude oil and enhancing oil recovery. To date, catalytic aquathermolysis which the catalyst was added into the oil floor at an interval when the high-temperature steam was injected, was of special significance in terms of the cost-effective exploration of heavy oil [2]. Since, Hyne *et al.* and Clark *et al.* [3] researched the details of the chemical reactions between steam, heavy oil, and Catalytic, it was found the addition of superheated steam and catalysts can help to upgrade the properties and compositions of heavy oil and bitumen thereby reacting with macromolecular components of heavy oil. Subsequently, a lot of efforts have been made to develop aquathermolysis catalysts and evaluate their upgrading effect [3]. For instance, Li *et al.* synthesised a new type of nano-nickel catalyst to upgrade and visbreak heavy oil [4]. Olvera *et al.* developed a NiWMoC nanocatalyst by mechanical mixing method to reduce the viscosity of heavy oil [5]. Chen *et al.* [6, 7] used K₃PMo₁₂O₄₀ with nano-Keggin structure and aromatic sulfonic H₃PMo₁₂O₄₀ as aquathermolysis catalysts to reduce the viscosity of a range of extra-heavy oils. Currently available aquathermolysis catalysts can be divided into five categories: water-soluble catalyst, oil-soluble catalyst, superacid catalyst, nanocatalyst and ionic liquid catalyst. However, The application of catalytic aquathermolysis in petroleum industry, greatly depended on the development of cheap and highly efficient catalysts. It still have shortcomings as the catalysts for aquathermolysis of heavy oil, because water-soluble solid nanocatalysts cannot be readily transferred from aqueous phase to oil phase, while oil-soluble solid nanocatalysts usually rely on organic compounds as the carrying agents.

Wasn't there a balanced approach? Did it ease the trouble? It was found that surface-modified SiO₂ accompanied by compatibility with oil well could be potential catalyst carrier, because they can be steadily dispersed in many organic mediums and easily carried by water and transferred into oil phase and fabricated from relatively low-priced precursors by hydrolysis-condensation reaction [8, 9].

In this research, surface-modified SiO₂ as carrier of catalyst, we prepared four kinds of phase transfer functional nanocatalysts: silica/zero valence iron (denoted as SiO₂/Fe), silica/zero valence iron and nickel (denoted as SiO₂/Fe/Ni), silica/metatitanic acid (denoted as SiO₂/H₂TiO₃) and silica/zirconia modified metatitanic acid (denoted as SiO₂/Zr/H₂TiO₃), and evaluated their catalysing performance for the aquathermolysis of two kinds of extra-heavy oil (viscosity at 50°C: 184,000 and 58,000 cp) produced at Shengli Oilfield (Dongying, China) thereby facilitating the recovering from the deep reservoirs at lowered 150°C. Moreover, the supported nanocatalysts have several potential advantages, such as: having function of phase transfer, being low-cost and protecting our environment, under an field oil well.

2. Experimental

2.1. Preparation of surface-modified SiO₂: Analytical pure reagents were used without further treatment. Surface-modified SiO₂ was prepared with in situ surface modification method [10].

2.2. Preparation of catalysts: Preparation of SiO₂/Fe catalyst: ferric chloride hexahydrate and surface modified silica (Jiyuan Wangwu Nano Technology Company Ltd; Jiyuan, China) were mixed at the same molar ratio and put into a 500 ml three-necked flask, followed by the addition of 200 ml of ethanol under 10 min of mechanical stirring to allow complete dissolution. Into the resultant solution was dropwise (rate: 1–2 ml/min) added 0.66 mol of sodium borohydride dissolved in 50 ml of deionised water through a constant pressure drop funnel under vigorous stirring [11, 12]. The reaction mixture was allowed to react for 2 h and then filtered. The filtered cake (black solid) was washed repeatedly with mixed solution of deionised water and alcohol, followed by vacuum-drying overnight and to obtain a SiO₂/Fe catalyst. SiO₂/Fe/Ni catalyst was fabricated in the same way while nickel chloride hexahydrate and ferric chloride hexahydrate were introduced as the source of nickel and iron.

Preparation of SiO₂/H₂TiO₃ catalyst: Titanium oxysulfate was dissolved in 200 ml of distilled water at a certain concentration. Into resultant solution was added the dispersion of surface-modified silica in ethanol under 30 min of vigorous stirring at room temperature. Then ammonia was dropwise added into the mixed solution to adjust the pH value to be about 8. The formed gel was transferred into a polytetrafluoroethylene lined autoclave and held at 160°C for 8 h to yield SiO₂/H₂TiO₃ nanocomposite. SiO₂/Zr/H₂TiO₃

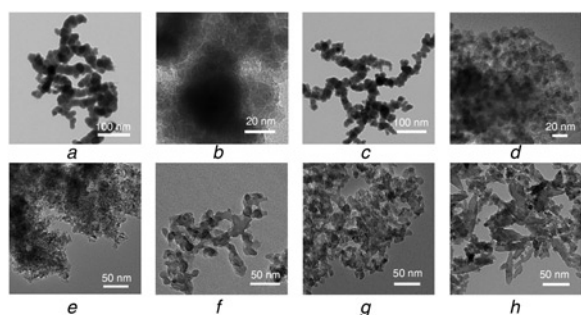


Fig. 1 TEM images of

- a Fe
- b SiO₂/Fe
- c Fe/Ni
- d SiO₂/Fe/Ni
- e H₂TiO₃
- f SiO₂/H₂TiO₃
- g Zr/H₂TiO₃
- h SiO₂/Zr/H₂TiO₃

was prepared in the same manners while zirconium nitrate pentahydrate and titanium oxysulfate were introduced as the source of zirconium and titanium.

2.3. Characterisation of catalysts: As-prepared catalysts were characterised by transmission electron microscopy (TEM; JEM 2010; JEOL, Japan), and Fourier transform infrared spectrometry (FTIR; AVATAR-360, Nigao Instrument Company, USA; wavenumber range 400–4000 cm⁻¹). The specific surface area was measured by Brunauer–Emmett–Teller (BET) method (JW-BK 222, Beijing JWB Science and Technology Company Ltd; Beijing, China).

2.4. Evaluation of catalysis performance of the catalysts for aquathermolysis reaction of heavy oil: The catalytic performance of the as-prepared phase transfer catalysts for the aquathermolysis reaction of two kinds of heavy oil samples [denoted as oil sample A (viscosity: 184,000 cP) and oil sample B (viscosity: 58,000 cP)] collected at Shengli Oilfield was evaluated with an LHG-3 high-pressure reactor (Dingda Machinery Company, Weihai, China). Briefly, 100 g of to-be-tested heavy oil, 50 g of deionised water and 1.0 g of as-prepared catalysts were placed into the LHG-3 high-pressure reactor in a batch. The reaction mixture was heated to 150°C and held there for 36 h to allow the completion of the aquathermolysis reaction. At the end of aquathermolysis reaction, the reaction mixture was cooled to room temperature naturally. The viscosities of the oil samples before and after aquathermolysis reaction were determined with a Brookfield DV-III programmable viscometer at 50°C. The ratio of the viscosity reduction is calculated as $\Delta\eta = (\eta_0 - \eta)/\eta_0 \times 100\%$, where $\Delta\eta$ (cP) is the viscosity reduction ratio of the heavy oil, η_0 (cP) is the viscosity of the original heavy oil, and η (cP) is the viscosity of the heavy oil after the catalytic aquathermolysis reaction. Furthermore, four groups of components including

saturated hydrocarbon, aromatic hydrocarbon, resin and asphaltene (denoted as SARA) were separated from the samples with a column chromatograph according to the Chinese Petroleum industrial standard SY/T 5119-2008 [13].

3. Results and discussion

3.1. Characterisation of as-prepared catalysts: Fig. 1 shows the TEM images of the as-prepared SiO₂/Fe, SiO₂/Fe/Ni, SiO₂/H₂TiO₃ and SiO₂/Zr/H₂TiO₃, and the TEM images of Fe, Fe/Ni, H₂TiO₃ and Zr/H₂TiO₃ are also presented for comparisons. It can be seen that Fe (Fig. 1a) and Fe/Ni (Fig. 1c) have a size of about 30 nm, bigger than SiO₂/Fe and SiO₂/Fe/Ni. The chain-like assemblies of Fe and Fe/Ni nanoparticles are due to strong magnetic dipole-dipole interaction between individual Fe and Fe/Ni. As to SiO₂/Fe and SiO₂/Fe/Ni, Fe³⁺ and Ni²⁺ are adsorbed on the surface of nanosilica, while methyl increases the steric hindrance of the nanoparticles; subsequently, the growth of the metal crystal nucleus is restricted (Figs. 1b and d). Pure H₂TiO₃ has a particle size of 20 nm and shows signs of severe agglomeration (Fig. 1e).

Since TiO₂²⁺ is present on the surface of nanosilica before the formation of H₂TiO₃ nanoparticles, the growth of H₂TiO₃ crystal nucleus is restricted during the formation of SiO₂/H₂TiO₃ (Fig. 1f). Pure Zr/H₂TiO₃ has a large particle size and uneven distribution (Fig. 1g); and SiO₂/Zr/H₂TiO₃ has a particle size of 20 nm and relatively uniform distribution, which is because the methyl increases the steric hindrance of the nanoparticles and restricts the growth of metatitanic crystal nucleus. In one word, the as-prepared catalysts loaded by nanosilica exhibit better dispersibility than the unloaded nanoparticles.

The specific surface area and total pore volume of the catalysts and unloaded nanoparticles, determined by the BET method, are listed in Table 1. The specific surface area of SiO₂ is 103.5 m²/g, and its total pore volume is 0.56 cm³/g, higher than the catalysts. This implies that, during the preparation of catalysts, newly generated nanoparticles are partly deposited on the surface of the silica and partly filled into the pores of the surface-modified silica as well. As a result, the catalyst exhibits a smaller specific surface area and total pore volume than pure silica. Meanwhile, It is noted that the specific surface area and total pore volume of the catalysts is upper than unloaded, to explain the catalyst possessing greater effective affecting acreage.

The FTIR spectra of surface-modified silica, SiO₂/Fe, SiO₂/Fe/Ni, SiO₂/H₂TiO₃ and SiO₂/Zr/H₂TiO₃ are shown in Fig. 2. The absorption bands at 1096 and 797 cm⁻¹ correspond to the anti-symmetric stretching vibration and bending vibration of Si–O–Si. The absorption bands at 3427 and 1634 cm⁻¹ are assigned to anti-symmetric and symmetric stretching vibration of O–H and bending vibration of H–O–H, and these bands confirm the presence of crystal water and adsorbed water in the as-prepared catalysts. Besides, the absorption peaks of –CH₃ and Si–CH₃ are located at 2966 and 845 cm⁻¹, which confirms that the coupling agent is bonded with the nanosilica surface by covalent bond. Moreover, the absorption bands of SiO₂/Fe, SiO₂/Fe/Ni, SiO₂/H₂TiO₃ and SiO₂/Zr/H₂TiO₃ at 2966, 845, 1096, and 797 cm⁻¹ are much weaker than the same absorption bands of surface-modified silica.

Table 1 Specific surface area and total pore volume of the catalysts and unloaded nanoparticles

Unloaded nanoparticles	Specific surface area, m ² /g	Total pore volume, cm ³ /g	Loaded catalysts	Specific surface area, m ² /g	Total pore volume, cm ³ /g
			SiO ₂	103.5	0.56
Fe	33.1	0.08	SiO ₂ /Fe	61.9	0.33
Fe/Ni	23.5	0.06	SiO ₂ /Fe/Ni	69.5	0.36
H ₂ TiO ₃	57.6	0.08	SiO ₂ /H ₂ TiO ₃	77.2	0.34
Zr/H ₂ TiO ₃	49.8	0.07	SiO ₂ /Zr/H ₂ TiO ₃	86.3	0.39

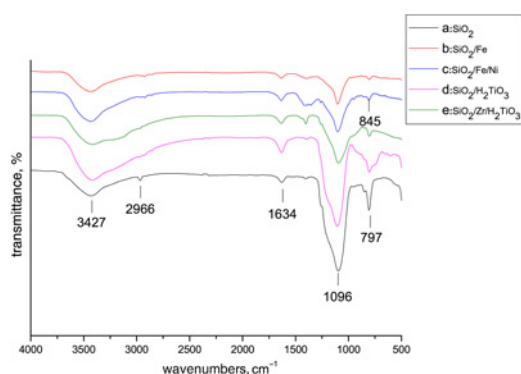


Fig. 2 FTIR spectra of surface-modified silica, SiO_2/Fe , $\text{SiO}_2/\text{Fe}/\text{Ni}$, $\text{SiO}_2/\text{H}_2\text{TiO}_3$ and $\text{SiO}_2/\text{Zr}/\text{H}_2\text{TiO}_3$

In this case, It is interesting to note that the supported catalyst by surface-modified silica can be successfully synthesised, corresponding to TEM, and BET.

3.2. Results of aquathermolysis experiments: We aim to attempt low temperatures, short time and relatively low dosage, to promising applications in the petroleum industry, the viscosity reduction rate of the tested heavy oil samples after 36 h of aquathermolysis reaction at 150°C in the presence of nanocatalysts with different dosages is presented in Fig. 3. When no catalyst is added in the reaction system, the viscosity of the two types of heavy oils reduces slightly after the aquathermolysis reaction, which indicates that, without the catalysts, high temperature steam alone exhibits very limited ability in reducing the viscosity of the heavy oils. When nanocatalysts are introduced

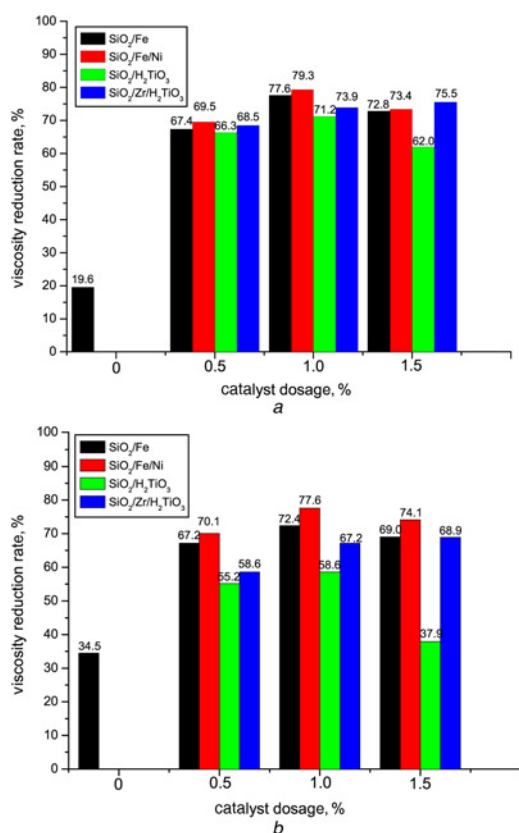


Fig. 3 Viscosity reduction rate of
a Heavy oil A (184,000 cP)
b Heavy oil B (58,000 cP) after 36 h of aquathermolysis reaction at 150°C in the presence of nanocatalysts with different dosages

Table 2 Saturated hydrocarbon, aromatic hydrocarbon, resin and asphalt (denoted as SARA) compositions of the tested heavy oils before and after aquathermolysis reaction

Sample	Constituent (mass fraction, %)			
	Saturated hydrocarbon	Aromatic hydrocarbon	Asphalt	Resin
heavy oil A	10.45	22.36	37.43	29.76
heavy oil B	19.03	28.83	26.42	25.72
heavy oil A + $\text{SiO}_2/\text{Fe}/\text{Ni}$	17.57	25.45	30.59	26.39
heavy oil B + $\text{SiO}_2/\text{Fe}/\text{Ni}$	25.67	30.04	19.98	24.31

into the aquathermolysis reaction system, the viscosity of the tested heavy oils tends to reduce gradually with the increase of the catalyst dosage; which is consistent with findings of Abarasi *et al.* [14]. The maximum viscosity reduction rate (79.3%) is obtained at a $\text{SiO}_2/\text{Fe}/\text{Ni}$ catalyst dosage of 1.0% [15]. Particularly, SiO_2/Fe and $\text{SiO}_2/\text{Fe}/\text{Ni}$ are more effective than $\text{SiO}_2/\text{H}_2\text{TiO}_3$ and $\text{SiO}_2/\text{Zr}/\text{H}_2\text{TiO}_3$ in reducing the viscosity of the two kinds of heavy oil. Moreover, when the dosage of the nanocatalysts is above 1.0%, elevating catalyst dosage has little influence on the viscosity of the tested heavy oil.

Table 2 lists the SARA composition of the tested heavy oils before and after aquathermolysis reaction. It can be seen that the asphalt composition of heavy oil A is larger than the one of heavy oil B, which is why heavy oil A has higher viscosity than heavy oil B. After 36 h of aquathermolysis reaction at 150°C in the presence of $\text{SiO}_2/\text{Fe}/\text{Ni}$ catalyst, the amounts of the saturated hydrocarbon and aromatic hydrocarbon are increased, while the amounts of resin and asphalt are decreased. This illustrates that the heavy components can be pyrolysed to form light components more easily upon catalytic aquathermolysis.

3.3. Formation mechanism of surface-modified silica: Analysing the mentioned TEM, FTIR, and BET data, we can describe the formation mechanism of phase transfer functional nanocatalysts (see Fig. 4). The in situ surface modification process of nanosilica with HMDS (Hexamethyldisilazan) is a condensation-like polymerisation process, and HMDS as the chain terminator prevents nanosilica from further agglomerating and changes the surface structure of nanosilica. Subsequently, because of the physical adsorption of nano- SiO_2 , ingredient solution of catalysts are adsorbed on the surface or in the pores of the silica. When the precipitating agent is dropwise added to the solution, the ingredient in the solution are hydrolysed to generate gel and are enwrapped on the surface of nano-silica. After the hydrothermal reaction, the gel is dehydrated to form grains that are attached to the surface of SiO_2 , to make the nanocatalysts. Because silica is surface-capped with methyl, the generated

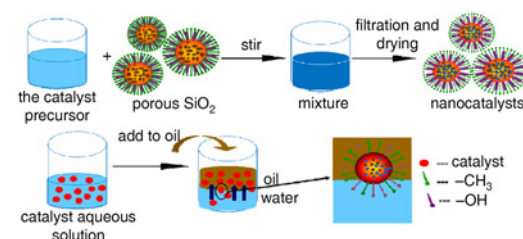


Fig. 4 Formation mechanism of phase transfer functional nanocatalysts

nanocatalysts exhibit lipophilicity. Moreover, the hydroxyl on silica surface adds to the dispersibility of the nanocatalysts in aqueous phase. When the as-prepared nanocatalysts are contacted with oil phase, they can be readily transferred from the aqueous phase into the oil phase, showing the so-called phase transfer function.

4. Conclusions: In summary, we have synthesised four kinds of phase transfer functional catalysts and investigated their catalytic performance for the aquathermolysis reaction of two kinds of heavy oils collected at Shengli Oilfield. Findings indicate that the as-prepared $\text{SiO}_2/\text{Fe}/\text{Ni}$ catalyst can reduce the apparent viscosity of the two kinds of heavy oils by 79.3 and 77.6% at a nanocatalyst mass fraction of 1%, an aquathermolysis reaction temperature of 150°C and an aquathermolysis time of 36 h. This is because, after the aquathermolysis reactions, the amounts of asphalt and resin of the tested heavy oils are decreased, while the amounts of the saturated and aromatic hydrocarbons are increased, due to the dissociation of C–R (R = S, N, O, C) bond. In view of the simple preparation and low-cost for synthesis, we anticipate that the as-prepared $\text{SiO}_2/\text{Fe}/\text{Ni}$ catalyst could find promising application in enhancing heavy oil recovery.

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6 References

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