

Preparation of silica-supported nanoFe/Ni alloy and its application in viscosity reduction of heavy oil

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Nanozero valent iron and nickel particles of silica composite (SiO₂/Fe/Ni) were prepared via sodium borohydride reduction of ferric chloride and nickel chloride mixed solution in the presence of surface-modified silica. The prepared nano-SiO₂/Fe/Ni was characterised by transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectrometry and Brunauer–Emmett–Teller specific surface area method. It was found that the SiO₂/Fe/Ni, composed of silica with an average size of about 12 nm and zero valent iron and nickel nanoparticles (Fe/Ni) with an average size of several nanometres, exhibited good anti-oxidation stability, dispersity and phase transfer function. The catalytic effect of SiO₂/Fe/Ni on the Shengli extra-heavy oil was evaluated at a low temperature and the sulphur content of heavy oil before and after aquathermolysis was analysed by an elemental analyser. Results have revealed that the SiO₂/Fe/Ni has good catalytic performance in the aquathermolysis process of heavy oils. In particular, at the condition of mass fraction of 0.5% and reaction temperature of 150°C for 48 h, it could significantly reduce the viscosity of heavy oil from 184 to 42 Pa·s. When compared with the original heavy oil sample the viscosity reduction rate was 77.17%, showing promising potential in the industrial production of heavy crude oils.

1. Introduction: Heavy oil makes up a large proportion of the oil and gas resources in the world, and the total resource reservoirs are approximately 1000×10^8 t. The confirmed and controlled heavy oil reservoirs in China are about 16×10^8 t, which is just less than Venezuela, Canada and America [1]. With the depletion of conventional crude reserves, heavy oil reservoirs are becoming increasingly important, and the production of heavy crude oil has reached approximately 4.7×10^6 t by Sinopec in 2010 with thermal recovery. According to the forecast of the U.S. Department of Energy, towards the middle of this century heavy oil will make up more than 50% of the world's energy supply.

However, it is very technically challenging to extract heavy oil in an economical and efficient manner, because of the high viscosity and composition complexity of heavy oil reservoirs. The high viscosity is the main reason for the difficult recovery and transportation of heavy oil, because of the high asphaltene and resin content. Currently, cyclic steam stimulation technology is the most popular and effective way of enhanced heavy oil recovery throughout the world, especially in China where approximately 80% of heavy oil resources were recovered in this way [2]. In the process, steam is injected into a reservoir to provide the heat that is required for visbreaking of the heavy oil/bitumen [3].

Hyne *et al.* [4] discovered that superheated steam could not only reduce the viscosity of heavy oil but also react with some components of heavy oil, thereby changing the properties and composition of heavy oils, and described the chemical reaction between high-pressure and high-temperature steam with the reactive components of heavy oil and bitumen as 'aquathermolysis'. With the addition of the catalyst, the efficiency of the aquathermolysis reactions and the viscosity reduction of heavy oil can be greatly increased. Clark *et al.* [5, 6] found that when aqueous metal species was added into the process, the viscosity of heavy oil was further reduced in comparison with steam-only experiments, and all of the first row transition metals possessed the catalytic property. Then, a number of various catalysts were studied to catalyse aquathermolysis. Wen *et al.* [7] and Zhang *et al.* [8] reported that the

polyoxometalates (H₄SiW₁₂O₄₀ and H₃PMo₁₂O₄₀) had synergetic effects with reservoir minerals in viscosity reduction of heavy oil. Fan *et al.* [9–12] investigated the feasibility of aquathermolysis of heavy oil under steam stimulation conditions, and they found that the synergetic effects of minerals and steam caused viscosity reduction as well as changing the composition of heavy oil. In a typical aquathermolysis reaction, water acts as both heat donor and hydrogen donor. However, Fan *et al.* [13] and Zhong *et al.* [14] demonstrated that the viscosity reduction was greatly enhanced with an appropriate hydrogen donor such as tetralin added to the aquathermolysis reaction. The expensive hydrogen donors such as tetralin and methyl-cyclohexane would likely not be economically utilized at the field scale.

Greff *et al.* [15] found that micrometal and nanometal catalysts could effectively lower the viscosity of heavy oil at 200°C, in the presence of microwave irradiation. Shokrlu *et al.* [16] studied the effect of viscosity reduction of heavy oil using micrometal and nanometal particles by simulating the steam stimulation processes. They found that the concentration, type and size of the particles were critically important to viscosity reduction. Considering the above research, the catalytic temperature was above 200°C, while only a small region was met downhole, which limited the catalytic aquathermolysis effect. In this reported work, a phase transfer functional nanoSiO₂/Fe/Ni catalyst was synthesised, which can be easily carried by water and transferred into the oil phase spontaneously downhole, and used for the aquathermolysis of Shengli extra-heavy oil at a low temperature range of 120–180°C.

2. Experimental

2.1. Reagents: The reagents used were ferric chloride hexahydrate (FeCl₃·6H₂O, AR, Tianjin Fengchuan Chemical Reagent Technology Company Ltd, Tianjin, China), nickel chloride hexahydrate (NiCl₂·6H₂O), sodium borohydride (NaBH₄, Tianji Fuyu Fine Chemical Company Ltd, Tianjin, China) and ethanol (C₂H₅OH, AR, Tianji Fuyu Fine Chemical Company Ltd, Tianjin, China). The reagents were purchased and used without further

treatment. The surface-modified silica was produced by Jiyuan Wangwu Nano Technology Company (Jiyuan, China) and the extra-heavy oil sample used was supplied by Shengli Oil Field (Dongying, China), the viscosity of which was 184 Pa·s at 50°C.

2.2. Preparation of the catalyst SiO₂/Fe/Ni: The SiO₂/Fe/Ni nanoparticles were prepared by a liquid-reduction route as before [17]: FeCl₃·6H₂O and NiCl₂·6H₂O were dissolved in 200 ml of ethanol and 0.18 mol surface-modified silica was dispersed in 200 ml of ethanol by ultrasound, and then the two solutions were mixed and transferred into a 1000 ml three-necked flask, with mechanical stirring for 30 min to obtain a homogeneous mixture. Subsequently, a specified quantity of NaBH₄, water and ethanol solution was added dropwise while the mixed solution in the flask was vigorously stirred under ambient temperature. The mixture finally became black, indicating the formation of SiO₂/Fe/Ni nanoparticles. Pure Fe/Ni alloy nanoparticles were prepared in the same way without the surface-modified silica.

2.3. Characterisation of the catalyst: Transmission electron microscopy (TEM, JEOL JEM-2010) was used to observe the morphology and size of the prepared nanoparticles. The specimen for TEM detection was prepared by depositing two droplets of dilute ethanol solution of the prepared SiO₂/Fe/Ni onto a carbon-coated Cu-grid (Ernest Fullam Inc., New York, USA). Then, the specimen was dried in a nitrogen atmosphere. The crystal structure of the nanoparticles was studied by X-ray diffraction (XRD; Bruker XRD D8 Advance diffractometer, Bruker Spectrum Instrument Company, Germany) with Cu K α radiation at 45 kV and 30 mA. The scan rate was 2.0°/min for the temperature range of 20°–60°. A proper amount of as-prepared SiO₂/Fe/Ni was mixed with a spectroscopically pure KBr matrix in an agate mortar and pressed into small discs; the Fourier transform infrared (FTIR) spectra were then recorded with a diffuse reflectance accessory connected to an AVATAR-360 FTIR spectrometer (Nigaoli Instrument Company, USA) in the wavenumber range of 400–4000 cm⁻¹. The classic Brunauer–Emmett–Teller (BET) isotherm method was used to determine the specific surface area of the SiO₂/Fe/Ni nanoparticles with a JW-BK 222 chemisorption surface area analyser (Beijing JWB Science and Technology Company Ltd, Beijing, China). The representative SiO₂/Fe/Ni sample was pre-dried in a vacuum desiccator at room temperature (20 ± 1°C) and then degassed at 90 and 200°C separately for 1 h. After that the sample was finally cooled to cryogenic temperature with liquid nitrogen and contained in a glass tube exposed to nitrogen gas at a series of precisely controlled pressures. When the saturated adsorption was reached, the reverse sequence of desorption occurred. The total surface area of the SiO₂/Fe/Ni nanoparticles was determined by taking into account the sorption and desorption of nitrogen gas. The sulphur content of heavy oil was measured by an organic elemental analyser (ThermoFisher Flash EA1112, Italy).

2.4. Catalytic aquathermolysis of heavy oil: The catalytic aquathermolysis tests were carried out in an LHG-3 high-pressure reactor (volume: 500 ml; initial pressure: atmospheric pressure). A measure of 100 g of heavy oil was first added into the reactor, and then 0.5 g of catalyst dispersed into 100 ml of deionised water was added. The air in the spare space of the reactor was replaced with nitrogen. Then the reactor was sealed and heated to 150°C in an XGRL-4A high-temperature roller furnace for aquathermolysis reaction at a rate of 2–3°C/min and a rolling rate of 10 rpm and held for 24 h. The reaction mixture was cooled to room temperature naturally and then put into a 200 ml beaker. The water in the heavy oil was then removed via a heavy oil quick dewaterer, thereby giving the to-be-tested heavy oil sample. The viscosity of the heavy oil samples was measured at 50°C with a Brookfield DV-III programmable viscometer.

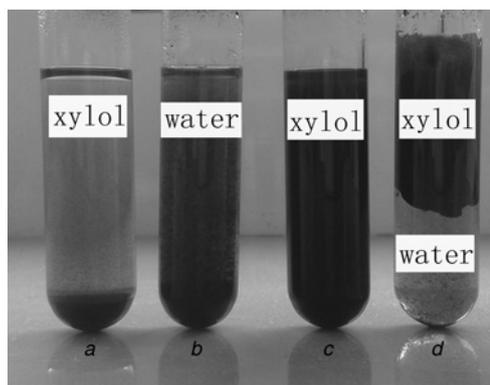


Figure 1 Dispersal of nano-SiO₂/Fe/Ni catalyst in various media
 a Fe/Ni in xylol
 b SiO₂/Fe/Ni in water
 c SiO₂/Fe/Ni in xylol
 d SiO₂/Fe/Ni dispersed in water and then xylol was added into the solution

Approximately 15 g of heavy oil was placed in the sample cup, heated and equilibrated for 30 min at 50°C by a thermosel heater, and the measurement was operated precisely according to the procedures. The rate of viscosity reduction was calculated according to the expression $\Delta\eta = (\eta_0 - \eta)/\eta_0 \times 100\%$, where $\Delta\eta$ (%) is the heavy oil viscosity reduction ratio before and after the catalytic reaction, η_0 (Pa·s) is the viscosity of the original heavy oil, and η (Pa·s) is the viscosity of the heavy oil after the catalytic aquathermolysis reaction.

3. Results and discussion

3.1. Characterisation of nanoSiO₂/Fe/Ni catalyst: The dispersal of nanoSiO₂/Fe/Ni catalyst is shown in Fig. 1. It is found that the catalyst can be well dispersed in both water (Fig. 1b) and various organic solvents (Fig. 1c) such as toluene, xylol or diesel oil, while the unsupported Fe/Ni nanoparticles cannot be dispersed in organic solvent (Fig. 1a). The surface of the SiO₂/Fe/Ni nanoparticles is in contact with water molecular, –OH and hydrophobic functional groups (proved by FTIR), which makes the catalyst disperse well in either water or organic solvents. However, if the organic solvent is added into the water-dispersed solution, the catalyst will rapidly transfer into the organic phase from the water phase spontaneously, showing phase transfer function and good lipophilicity (Fig. 1d).

Fig. 2 shows the TEM images of the prepared SiO₂/Fe/Ni nanoparticles. The unloaded nanoscale Fe/Ni nanoparticles (Fig. 2a) were spherical and the particle size ranged from 20 to 30 nm. The chain-like assemblies of Fe/Ni nanoparticles were due to the strong magnetic dipole–dipole interaction between individual Fe/Ni nanoparticles [18, 19]. The surface-modified silica particles had an average size of 12 nm (Fig. 2b). The Fe³⁺ and Ni²⁺ were absorbed and reduced into the pore or on the surface of the nano-silica, which restricted the growth of the crystal nucleus of the

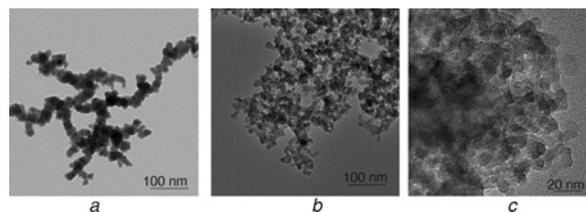


Figure 2 TEM images of
 a Fe/Ni
 b SiO₂
 c SiO₂/Fe/Ni nanoparticles

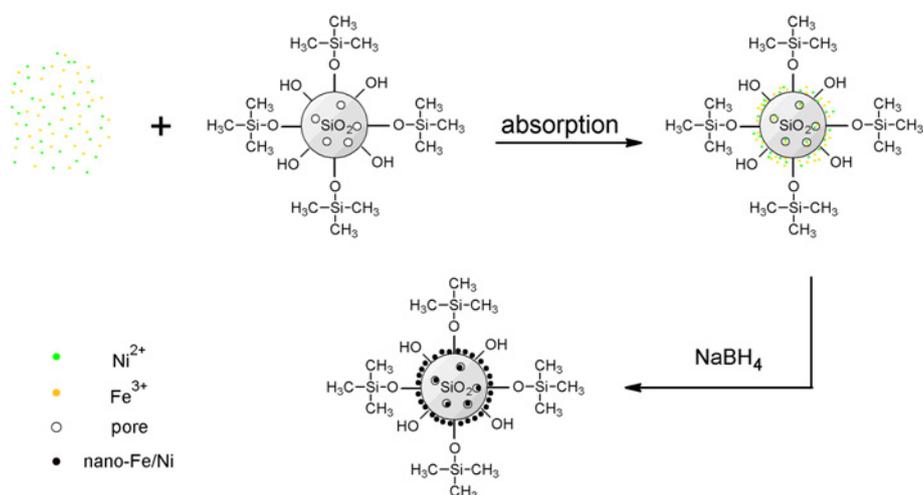


Figure 3 Formation mechanism of $\text{SiO}_2/\text{Fe/Ni}$ transfer functional nanoparticles

metal, so the average size of nanoFe/Ni on the surface of silica was only several nanometres (Fig. 2c).

The specific surface area of the Fe/Ni, $\text{SiO}_2/\text{Fe/Ni}$ and the surface-modified silica, determined by the BET method, was 23.5, 69.5 and 103.5 m^2/g ; and their total pore volume was 0.06, 0.36 and 0.56 cm^3/g , respectively. The results demonstrated that during the preparation of $\text{SiO}_2/\text{Fe/Ni}$, Fe^{3+} and Ni^{2+} were adsorbed and reduced directly into the pores and on the surface of the modified silica nanoparticles, when the NaBH_4 solution was added. Therefore, the synthesised Fe/Ni nanoparticles were deposited on the surface and also partially filled into the silica pores. As a result, the $\text{SiO}_2/\text{Fe/Ni}$ catalyst exhibited a smaller specific surface area and total pore volume than pure silica. Analysing the dispersal experiments, TEM images and BET analysis, we described the formation mechanism of the $\text{SiO}_2/\text{Fe/Ni}$ nanoparticles as shown in Fig. 3.

Fig. 4 shows the FTIR spectra of surface-modified silica (Fig. 4a), nanoscale Fe/Ni (Fig. 4b) and $\text{SiO}_2/\text{Fe/Ni}$ (Fig. 4c). The absorption bands at 3427 and 1634 cm^{-1} were assigned to anti-symmetric and symmetric stretching vibration of O–H and bending vibration of H–O–H [20], which confirm the presence of crystal water and adsorbed water in the $\text{SiO}_2/\text{Fe/Ni}$ phase transfer functional catalyst. The strongest peak (in Figs. 4a and c) corresponding to the anti-symmetric stretching vibration of Si–O–Si was observed at 1096 cm^{-1} , and the absorption bands at 470 and 797 cm^{-1} were assigned to symmetric stretching vibration and bending vibration of Si–O–Si, respectively. The absorption peaks of $-\text{CH}_3$ and Si– CH_3 in Fig. 4a. were located at 2966 and 845 cm^{-1} , which

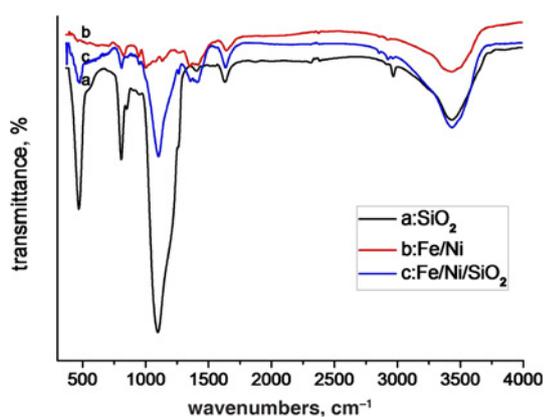


Figure 4 FTIR spectra of SiO_2 , Fe/Ni and $\text{SiO}_2/\text{Fe/Ni}$ nanoparticles

confirmed that the surface of the silica was bonded with coupling agents by covalent bonds. Moreover, the absorption bands of $\text{SiO}_2/\text{Fe/Ni}$ in Fig. 4c, at 2966, 845, 1096, 797 and 470 cm^{-1} were much weaker than the same absorption bands of surface-modified silica, which proved that the Fe/Ni nanoparticles were deposited on the surface or pores of silica, corresponding to the TEM images and BET analysis.

The XRD pattern of $\text{SiO}_2/\text{Fe/Ni}$ is shown in Fig. 5. The diffraction peak at $2\theta = 45.0^\circ$ is assigned to FeNi_3 alloy, and the size of crystalline Fe/Ni is about 2 nm, calculated by the Scherrer equation. No diffraction peaks of iron oxide or nickel oxide are observed, which indicates that the as-prepared $\text{SiO}_2/\text{Fe/Ni}$ catalyst exhibits good anti-oxidation ability.

3.2. Catalytic evaluation of $\text{SiO}_2/\text{Fe/Ni}$ for heavy oil aquathermolysis: The effect of the catalyst type and reaction temperature on the viscosity of heavy oil undergoing 24 h of aquathermolysis tests is presented in Table 1. With no catalyst introduced into the reaction system, the viscosity of heavy oil was reduced to some extent, which implied that the chemical reaction happened between water and heavy oil, in this case with a temperature range of 120–180°C. When the $\text{SiO}_2/\text{Fe/Ni}$ catalyst was added, the viscosity reduction ratio could be significantly improved. However, pure Fe/Ni nanoparticles displayed a converse property of the catalyst, which increased the viscosity of heavy oil compared with blank experiments, possibly because they competed with heavy oil to react with steam. The reason

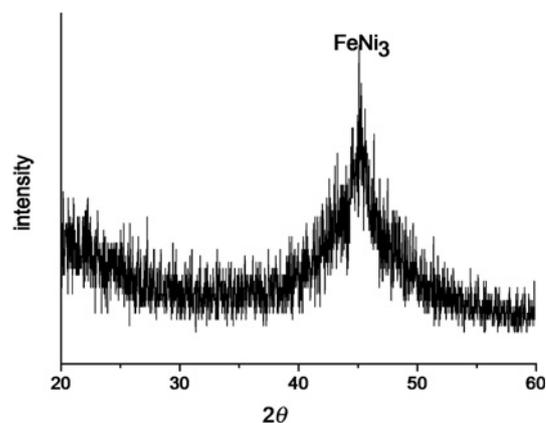


Figure 5 XRD pattern of $\text{SiO}_2/\text{Fe/Ni}$ nanoparticles

Table 1 Effect of catalyst type and temperature on viscosity reduction of heavy oil at 24 h

Reaction temperature, °C	Catalyst type	Viscosity, Pa·s	Viscosity reduction ratio, %
120	–	116	36.96
120	Fe/Ni	152	17.39
120	SiO ₂ /Fe	84	54.35
120	SiO ₂ /Fe/Ni	98	46.74
150	–	148	24.32
150	Fe/Ni	148	24.32
150	SiO ₂ /Fe	80	56.52
150	SiO ₂ /Fe/Ni	72	60.87
180	–	72	60.87
180	Fe/Ni	96	47.83
180	SiO ₂ /Fe	66	64.13
180	SiO ₂ /Fe/Ni	48	73.91

why the SiO₂/Fe/Ni catalyst had a better catalytic effect than pure Fe/Ni nanoparticles at the same reaction conditions was the smaller average size and higher lipophilicity of Fe/Ni after loading onto the hydrophobic silica. Therefore, the SiO₂/Fe/Ni could be transferred and dispersed well into the oil phase, which improved the efficiency of aquathermolysis effectively, with a viscosity reduction ratio of 73.91% at 180°C for 24 h. The SiO₂/Ni/Fe had a better catalytic effect than SiO₂/Fe because of the introduction of nickel, the viscosity reduction of which was enhanced from 64.13 to 73.91% at 180°C. The effect of SiO₂/Fe/Ni reaction time on viscosity of heavy oil at 150°C is shown in Table 2. It was discovered that the viscosity gradually reduced with extended reaction time, which had the same effect as increasing temperature. The viscosity reduction was more efficient for 48 h under 150°C than 180°C under 24 h, and then as the reaction time prolonged, the viscosity reduction ratio of heavy oil did not increase, which indicated that the catalytic reaction reached the equilibrium after 48 h. Moreover, the sulphur content of heavy oil was reduced from 1.77 to 1.25% after 48 h at 150°C.

According to organic chemistry theory and catalytic theory, the transition metal species have catalytic effects on organic hydrogenation and desulphurisation. Viscosity reduction of heavy oil requires decomposition of large molecules, such as asphaltene and resin molecules. During aquathermolysis of the tested heavy oil in the presence of a SiO₂/Fe/Ni catalyst, the metal species in the catalyst can react with the sulphur contained in the heavy oil to form the active catalyst species, thereby facilitating the dissociation of C–S bonds even at a relatively low temperature, since the C–S bond exhibits a lower dissociation energy than the C–C and C–H bonds. As the aquathermolysis reaction is conducted under a high enough temperature (150 and 180°C) and/or for a long enough reaction duration (48 h), the decomposition of the tested heavy oil will be accelerated in association with the dissociation of the C–C bond and even the C–H bond, thereby providing a much higher viscosity reduction ratio. In addition, even in the absence of steam, some metal nanoparticles may still function to reduce the viscosity of heavy oil [21], which implies that some chemical reactions independent of the aquathermolysis process may occur between the metal nanoparticles and heavy oil.

Table 2 Effect of SiO₂/Fe/Ni reaction time on viscosity of heavy oil at 150°C

Reaction time, h	12	24	36	48	72
Viscosity, Pa·s	102	72	58	42	44
Viscosity reduction ratio %	44.56	60.87	68.48	77.17	76.09

4. Conclusions: From the experimental results and analysis, the following conclusions are made:

(i) The SiO₂/Fe/Ni nanocatalyst was synthesised readily through liquid-phase reduction in the presence of surface-modified silica as a support. The prepared SiO₂/Fe/Ni catalyst consists of silica with an average size of about 12 nm and zero valent iron and nickel alloy nanoparticles with an average size of several nanometres.

(ii) The SiO₂/Fe/Ni nanocatalyst has the phase transfer function that it can transfer from the water to the oil phase spontaneously. Therefore, it can be carried underground by water and catalyse the heavy oil after being transferred into the oil phase.

(iii) The SiO₂/Fe/Ni catalyst exhibits better catalytic performance for the aquathermolysis process of heavy oils than unsupported Fe/Ni nanoparticles. The sulphur content of heavy oil is reduced from 1.77 to 1.25%, which proved the C–S bond visbreaking mechanism. Particularly with a dosage of 0.5%, the catalyst can drastically reduce the viscosity of the tested heavy oil from 184 to 42 Pa·s at 150°C, the temperature which can be easily met in the steam injection process, showing promising potential in the industrial production of heavy crude oils.

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