



Synthesis of silica/metatitanic acid nanocomposite and evaluation of its catalytic performance for aquathermolysis reaction of extra-heavy crude oil

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ABSTRACT

A lipophilic silica/metatitanic acid (denoted as SiO₂/H₂TiO₃) nanocomposite was synthesized by hydrothermal reaction with surface-modified SiO₂ as the lipophilic carrier. As-synthesized SiO₂/H₂TiO₃ nanocomposite was used as a catalyst to promote the aquathermolysis reaction of extra-heavy crude oil thereby facilitating the recovering from the deep reservoirs at lowered temperature. The catalytic performance of the as-synthesized SiO₂/H₂TiO₃ catalyst for the aquathermolysis reaction of the heavy oil at a moderate temperature of 150 °C was evaluated in relation to the structural characterizations by TEM, FTIR, XRD and FESEM as well as the determination of the specific surface area by N₂ adsorption–desorption method. Findings indicate that as-synthesized SiO₂/H₂TiO₃ nanocomposite exhibits an average size of about 20 nm as well as good lipophilicity and dispersibility in various organic solvents; and it shows good catalytic performance for the aquathermolysis reaction of the extra-heavy oil extracted from Shengli Oilfield of China. Namely, the as-synthesized SiO₂/H₂TiO₃ catalyst is capable of significantly reducing the viscosity of the tested heavy oil from 58,000 cP to 16,000 cP (referring to a viscosity reduction rate of 72.41%) at a mass fraction of 0.5%, a reaction temperature of 150 °C and a reaction time of 36 h, showing potential application in downhole upgrading heavy crude oils.

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1. Introduction

With the depletion of conventional crude oil, abundant heavy oil and oil sand as important hydrocarbon resources are increasingly attracting interest worldwide. The confirmed and controlled heavy oil reservoir in China has reached about 16×10^8 ton, less than that in Venezuela, Canada and USA [1]. However, the high viscosity and solidification of heavy oil and oil sand challenge their exploitation and transportation, and the recovery of the heavy oils is infeasible unless their viscosity is drastically reduced. To deal with this issue, researchers have developed many techniques including thermal recovery and cold production technology to promote heavy oil exploitation [2–5]. Among a variety of such techniques, steam stimulation is one of the most popular and effective technology for enhancing heavy oil recovery throughout the world, and it currently covers the recovery of approximately 80% of the heavy oil resources in China.

Hyne and co-workers [6,7] discovered that superheated steam could not only reduce the viscosity but also react with some components of heavy oil thereby changing the properties and upgrading heavy oil and oil sand. More importantly, they found that the addition of catalysts helps to greatly increase the efficiency of aquathermolysis reaction and provide greater viscosity reduction of heavy oil. Recently many researches on aquathermolysis have been carried out [8–11], and some achievements of catalytic aquathermolysis have been obtained in oilfield tests [12–15]. Zhong et al. [16] used water soluble metal ions (Fe²⁺, Cu²⁺, Al³⁺, Ni²⁺, Co²⁺, Mo²⁺, Zn²⁺, and Mn²⁺) as aquathermolysis catalysts to reduce the viscosity of extra-heavy oil at Liaohe Oilfield of China. Li et al. [17] found that the organic complexes of Fe³⁺ and Cu²⁺ as aquathermolysis catalysts can reduce the viscosity of the tested heavy oil at a rate of nearly 90%. Unfortunately, commonly used water-soluble aquathermolysis catalysts, due to poor compatibility with heavy oil, usually exhibit poor catalytic efficiency. Most of oil-soluble aquathermolysis catalysts (i.e., organometallics), though possessing better compatibility with heavy oil than the water-soluble counterparts, often rely on some organic solvents such as toluene and diesel oil as the carriers, which is less cost-effective and may cause environmental pollution as well.

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Dispersed nanocatalysts, due to their high specific surface area and active surface sites, have obtained comprehensive research in petroleum industry [18,19]. Shokrlu and Babadagli [20] reported that some micro and nano metal particles are able to reduce the viscosity of heavy oil and oil sand subjected to simulated steam stimulation processes, but nano metal particles are liable to oxidation in atmosphere and lose catalytic activity, which limits their application in oil field exploitation. Jing et al. [21] found that modified $\text{SO}_4^{2-}/\text{ZrO}_2$ solid super acids have good catalytic performance on viscosity reduction of heavy oil, but the presence of water associated with aquathermolysis is harmful to their catalytic activity. Wen et al. and Zhang et al. demonstrated that polyoxometalates have catalytic performance on the viscosity reduction of heavy oil within the proximate condition of steam stimulation processes [22,23]. However, the expensive polyoxometalates are less competitive in terms of the application at oilfield.

Viewing the above-mentioned researches all pre-set the catalytic temperature to be above 200 °C while the temperature of most of heavy oil reservoirs is below 150 °C, in the present research we pay special attention to the catalytic aquathermolysis at lowered temperatures of 120–180 °C. This paper reports the synthesis and structural characterization of lipophilic silica/metatitanic acid (denoted as $\text{SiO}_2/\text{H}_2\text{TiO}_3$) nanocomposite as well as the evaluation of its catalytic performance for the aquathermolysis reaction of the extra-heavy oil extracted from Shengli Oilfield.

2. Experimental

2.1. Reagents

Titanium oxysulfate-sulfuric acid hydrate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, synthesis grade; Aladdin Industrial Corporation; Shanghai, China), sulfuric acid (H_2SO_4 , analytical grade; Luoyang Haohua Chemical Reagent Company Ltd.; Luoyang, China), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, analytical grade; Kaifeng Zhongtian Chemical Company Ltd.; Kaifeng, China), and ethanol ($\text{C}_2\text{H}_5\text{OH}$, analytical grade; Tianjin Fuyu Fine Chemical Company Ltd.; Tianjin, China) were commercially obtained and used without further treatment. Surface-modified silica was produced by Jiyuan Wangwu Nano Technology Company (Jiyuan, China), and extra-heavy oil sample (viscosity at 50 °C: 58,000 cP) was supplied by Shengli Oilfield.

2.2. Preparation of $\text{SiO}_2/\text{H}_2\text{TiO}_3$ nanocomposite

A proper amount of titanium oxysulfate was dissolved in 200 mL of distilled water. The dispersion of surface modified silica was added into resultant solution under 30-min vigorous stirring at room temperature. Then ammonia was dropwise added into the mixed solution to adjust the pH value to be about 8 and initiate hydrolysis affording a gel. As-formed gel was transferred into a polytetrafluoroethylene lined autoclave and held at 160 °C for 8 h to yield hydrophobic $\text{SiO}_2/\text{H}_2\text{TiO}_3$ nanocomposite. Hydrophilic metatitanic acid (H_2TiO_3) was prepared in the same manners while no surface-modified silica was introduced.

2.3. Catalytic aquathermolysis tests of heavy oil

Catalytic aquathermolysis tests of the tested heavy oil were carried out in an LHG-3 high pressure reactor. Briefly, 100 g of the heavy oil and 0.5 g of the as-prepared catalyst dispersed in 100 mL of deionized water were sequentially added into the reactor. Then the reactor was sealed and heated to 150 °C at a rate of 2–3 °C/min in an XGRL-4A high temperature roller furnace to start aquathermolysis reaction at a rolling rate of 50 rpm and for duration of 24 h. Upon completion of the aquathermolysis reaction, the reaction mixture was naturally cooled

to room temperature and then transferred into a 200-mL beaker, followed by high speed centrifugation to remove residual water and afford the heavy oil sample ready for structural characterization and viscosity measurements.

2.4. Characterization of catalyst and heavy oil

A transmission electron microscope (TEM; JEM-2010, JEOL, Japan) was performed to observe the morphology and size of the as-prepared H_2TiO_3 and $\text{SiO}_2/\text{H}_2\text{TiO}_3$ catalysts. The crystal structure of the products was analyzed by X-ray diffraction (XRD; Bruker Spectrum Instrument Company, Germany), and the XRD patterns were recorded at a scan rate of $0.02^\circ/\text{s}$ over the 2θ range of 10° – 90° with $\text{Cu-K}\alpha$ radiation (40 kV and 40 mA) as the excitation source. The surface elements of $\text{SiO}_2/\text{H}_2\text{TiO}_3$ nanocomposite were tested by Field Emission Scanning Electron Microscope (FESEM; Nova NanoSEM 450, Holland) through EDAS model. The organic species adsorbed on the surface of the as-prepared $\text{SiO}_2/\text{H}_2\text{TiO}_3$ catalyst were analyzed with an AVATAR-360 Fourier transform infrared spectrometer (FTIR; Nicolet Instrument Company, USA). The as-synthesized catalyst was dried at 110 °C for 10 h and pressed into pellete with KBr, and then the FTIR spectra were recorded in the wavenumber range of 400–4000 cm^{-1} . A JW-BK 222 chemisorption surface area analyzer (Beijing JWB Science & Technology Company Ltd.; Beijing, China) was performed to determine the specific surface area of the as-prepared $\text{SiO}_2/\text{H}_2\text{TiO}_3$ catalyst by classic BET (Brunauer–Emmett–Teller isotherm) method. The viscosity of the heavy oil samples before and after aquathermolysis tests was measured with a Brookfield DV-3 programmable viscometer at 50.00 °C. Approximately 15 g of the heavy oil was placed in the sample cup, heated with a Brookfield thermosel heater and equilibrated at 50.00 °C for 30 min. The viscosity reduction rate is calculated as $\Delta\eta = (\eta_0 - \eta)/\eta_0 \times 100\%$, where $\Delta\eta$ (%) is the viscosity reduction rate 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.

The saturate, aromatic, resin and asphaltene (denoted as SARA) fractions of the tested heavy oil sample were determined by column chromatography according to the Industrial Specification of China Petroleum Standard SY/T 5119-2008 [24]. The asphaltenes were precipitated with *n*-hexane, and then the solution was concentrated and separated by a silica gel and neutral Al_2O_3 column. The saturated hydrocarbon in the concentrated solution was separated by *n*-hexane, and the aromatic hydrocarbon was separated by the mixed solution of dichloromethane and anhydrous ethanol. Furthermore, the resin was separated by trichloromethane.

3. Results and discussion

The dispersity of $\text{SiO}_2/\text{H}_2\text{TiO}_3$ in water and xylol is shown in Fig. 1. As-prepared $\text{SiO}_2/\text{H}_2\text{TiO}_3$ nanocomposite exhibits high hydrophobicity and good dispersity in organic solvents such as dimethylbenzene (xylol), toluene and diesel oil, which indicates that the nanocomposite possesses lipophilicity. This is because the surface-modified silica is highly hydrophobic and provides the $\text{SiO}_2/\text{H}_2\text{TiO}_3$ nanocomposite with good dispersibility in organic phase like heavy crude oil.

Fig. 2 presents the TEM images of pure H_2TiO_3 , surface-modified SiO_2 , and $\text{SiO}_2/\text{H}_2\text{TiO}_3$ nanocomposite. It is seen that pure H_2TiO_3 , with a particle size of 20–30 nm, has irregular shape (Fig. 2a). The average size of $\text{SiO}_2/\text{H}_2\text{TiO}_3$ nanocomposite and surface-modified silica particles are about 20 nm (Fig. 2c) and 12 nm (Fig. 2b) respectively. Since TiO^{2+} tends to be absorbed and precipitated in the pore or on the surface of nanosilica before the formation of H_2TiO_3 nanoparticles, the growth of H_2TiO_3 crystal nucleus is restricted. As a result, H_2TiO_3 nanoparticles formed on the surface or in the pores of the nanosilica exhibit an average size of only several nanometers (Fig. 2c).

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