



Enhanced pyrolysis and oxidation of asphaltenes adsorbed onto transition metal oxides nanoparticles towards advanced in-situ combustion EOR processes by nanotechnology



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ABSTRACT

The effects of redox activity of transition metal oxides nanoparticles on the kinetics of pyrolysis and oxidation of asphaltenes adsorbed onto the metal oxides surfaces were studied. Co_3O_4 , NiO, CuO, Mn_2O_3 , Fe_2O_3 , and WO_3 nanoparticles were synthesized and characterized by BET, XRD, FESEM, HRTEM, H_2 -TPR, and O_2 -TPD techniques. Asphaltenes were extracted from a heavy oil sample and adsorbed onto the metal oxides and fumed silica. The asphaltenes adsorption capacity (in mg/m^2) of the nanoparticles decreases in the order of $\text{NiO} > \text{Fe}_2\text{O}_3 > \text{WO}_3 > \text{Mn}_2\text{O}_3 > \text{CuO} > \text{Co}_3\text{O}_4 > \text{silica}$. The off gases of temperature programmed pyrolysis and oxidation (TPP and TPO, respectively) of the adsorbed asphaltenes were analyzed by an on-line FTIR equipped with a gas cell. TPP of the adsorbed asphaltenes on NiO with the highest adsorption capacity indicates that the coke formation increases by 11%, as compared to virgin asphaltenes, improving in-situ combustion process. TPO profiles of the asphaltenes, either virgin or adsorbed onto the surfaces, exhibit a low- and a high-temperature peak. The spreading role of the silica surface lowers the TPO low-temperature peak by about 100°C , compared to that of the virgin asphaltenes. While catalytic oxidation of the asphaltenes by the metal oxides shifts both low- and high-temperature TPO peaks by about 100 – 150°C to lower temperatures. Furthermore, kinetics of carbon oxides evolution during TPO of the asphaltenes was formulated by power-law grain model. The calculated activation energy for the asphaltenes oxidation over the nanoparticles increases in the order of $\text{Co}_3\text{O}_4 < \text{NiO} < \text{CuO} \approx \text{Mn}_2\text{O}_3 < \text{Fe}_2\text{O}_3 < \text{WO}_3$. The higher the redox activity of the metal oxides, the lower is the activation energy.

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1. Introduction

Large quantities of heavy oil reserves exist in the world but their production and recovery are often accompanied by severe difficulties. Heavy oils are categorized by their high viscosities (higher than 100 mPa s) and low API gravities (lower than 20° API) [1]. The high viscosity of heavy oils arises primarily from intermolecular interactions of especially large molecules such as asphaltenes, the heaviest and most polar components of heavy oils [2]. Owing to their high viscosities, the effective recovery of heavy oils by the conventional techniques suitable for light crude oils exploitation is not possible. Both primary production (pressure depletion) and secondary techniques (water flooding) together recover around 40%

of the original-oil-in-place of a petroleum reservoir [3]. In order to recover heavy oils especially from partially-depleted reservoirs, tertiary enhanced oil recovery (EOR) techniques were developed. Highly efficient heat utilization and displacement drive mechanism of heavy oils are the characteristics of in-situ combustion as a tertiary EOR process [4]. Successful in-situ combustion processes could recover almost up to 85% of the original-oil-in-place of a heavy oil-bearing reservoir and result in an upgrading of 5–7 API points for the reservoir oils [5].

In-situ combustion/fire flooding within a reservoir is induced by injection of air/enriched air and burning of a small portion of the reservoir oil in order to drive and thus recover the unburned fraction [6]. Exothermic oxidation reactions between hydrocarbons and oxygen result in a great increase in the temperature of heavy oils which leads to a significant decrease in the viscosity of the oils and thereby a considerable decline in the fluids flow resistances within the reservoirs [4–7]. The combustion front is very

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thin, no more than several inches, within which oxygen reacts with the solid carbonaceous residues (coke) deposited on the reservoir rock giving rise to temperatures of up to 700 °C [4]. The coke-like residue is designated as the fuel for in-situ combustion and is the product of hydrocarbons pyrolysis in the cracking/vaporization zone formed just downstream of the combustion front in a forward in-situ combustion [7]. Under the effect of heat, in the cracking/vaporization zone, pyrolysis reactions including cracking, dehydrogenation, and condensation lead to evolution of light gases and formation of the fuel [4,5]. According to the report by Verkoczy [8], asphaltenes have a significant contribution to the fuel formation during in-situ combustion process. When heated in the absence of oxygen, asphaltenes aggregates swell up and decompose leading to the formation of the coke-like deposits. A stable combustion front is one of the characteristics of a successful in-situ combustion process. The stability of the combustion front is controlled strongly by the reactivity of the deposited fuel and the rate of fuel deposition in the cracking/vaporization zone downstream of the combustion front [5,7]. In order to optimize the deposition rate of the coke-like residues and conduct a stable high-temperature combustion front, adsorptive removal followed by enhanced oxidation of asphaltenes by nanomaterials seems to be a feasible solution.

The development of an advanced in-situ combustion EOR process by nanotechnology is of significant importance since it has potential applications to efficient production and in-situ upgrading of the oil trapped within the whole spectrum of heavy oil reservoirs. The size of asphaltenes aggregates in the reservoir oils is within 5–20 nm depending on the composition of the oils and the reservoir conditions [9]. Nanomaterials are found to offer an appropriate activity and selectivity towards adsorption and catalytic conversion of the asphaltenes nanoaggregates [10–14]. In addition, nanoparticles are much smaller than pore spaces of reservoir rocks; thus they are found to be effectively transportable in porous media [15]. Upon adsorption of asphaltenes, nanoparticles become more stably suspended in reservoir oils and are expected to readily flow within the reservoirs. More recently, the adsorptive removal of asphaltenes from heavy oil model solutions by acid/base metal oxides nanoparticles was reported to be feasible [10]. Utilizing their lattice oxygen, transition metal oxides are supposed to oxidize/gasify a considerable portion of the adsorbed asphaltenes even in the absence of gas-phase oxygen and at relatively low temperatures, similar to the conditions of the cracking/vaporization zone formed in a successful in-situ combustion process. In addition, enhanced oxidation of the pyrolyzed asphaltenes on the surface of the metal oxides is expected in the presence of gas-phase oxygen and at high temperatures, typical of the combustion front conditions. Therefore, the metal oxides nanoparticles, with high oxygen storage capacities, are expected to involve in oxidation/gasification of adsorbed asphaltenes in the cracking/vaporization zone and then be re-oxidized in the combustion front and accelerate the complete oxidation of the coke-like residues.

Asphaltene adsorption and gasification/oxidation over metal oxides nanoparticles were reported to be effective for in-situ upgrading of reservoir oils [11,12]. The activity of transition metal oxides for asphaltene adsorption/oxidation decreases in the order of NiO > Co₃O₄ > Fe₃O₄ [13]. Nassar et al. investigated the isothermal oxidation of asphaltene adsorbed onto commercial metal oxides and observed diminished activation energies and enhanced oxidation rates over the nanoparticles compared to those for virgin asphaltene [14]. There is not a general consensus about the catalytic effects of metal oxides nanoparticles on the oxidation of adsorbed asphaltene [16,17]. Several reports attributed the lower activation energy for oxidation of adsorbed asphaltene to the catalytic role played by the metal oxides [11–14,16]. However, Abu Tarboush and Husein ascribed the oxidation features of adsorbed

asphaltene to the spreading role played by the nanoparticles surfaces, providing enhanced exposure of the adsorbed asphaltene to gas-phase oxygen [17]. Thermogravimetry, without analysis of released gases, is the widely-used technique by the researchers in the field of asphaltene oxidation, making the differentiation between the catalytic effects and surface roles of metal oxides almost unfeasible.

In this work, temperature-programmed oxidation (TPO) coupled with Fourier transform infrared spectroscopy analysis of released gases is employed for the first time to study the oxidation kinetics of asphaltene adsorbed onto transition metal oxides nanoparticles. Asphaltene is extracted and their thermal oxidation is studied. The asphaltene is then adsorbed onto the surfaces of transition metal oxides (with redox activity) and fumed silica (with no redox activity) and oxidation of the adsorbed asphaltene is investigated. Furthermore, the asphaltene, either virgin or adsorbed, are pyrolyzed in Ar and then their post-pyrolysis oxidation features are studied. Finally, carbon oxides evolution during oxidation of the asphaltene is formulated.

2. Experimental

2.1. Synthesis and characterization of metal oxides nanoparticles

Six different types of transition metal oxides comprising Co₃O₄, NiO, CuO, Mn₂O₃, Fe₂O₃, and WO₃ were synthesized by a simple precipitation method. Aqueous solutions containing 0.05 M of Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Mn(NO₃)₂·4H₂O, Fe(NO₃)₃·9H₂O, or Na₂WO₄·2H₂O (all high purity salts from Merck) were prepared. Each metal cation was titrated under vigorous mixing by dropwise addition of stoichiometric quantities of 5.0 M ammonia solution (Merck) for 40 min. For precipitation of (WO₄)²⁻ anion, 5.0 M nitric acid solution (Merck) was employed and the synthesis reaction proceeded with the molar ratio of (WO₄)²⁻/H⁺ = 1/2. The precipitation syntheses were conducted at 60 °C with continuous stirring at 400 rpm for 12 h in a sealed beaker. The syntheses pH was fixed at 10 except for WO₃ which was synthesized at pH = 1; therefore, during the syntheses, extra amounts of the ammonia or nitric acid solution were added whenever the pH was required to be adjusted. After complete precipitation, the solutions were left to cool down, and then centrifuged at 5000 rpm for 10 min. The precipitates were washed with plenty of DI water and centrifuged to achieve neutral pH. Finally, the samples were washed with ethanol (Merck), dried at 80 °C overnight, and then calcined at 500 °C in air for 4 h.

The crystalline structure of the nanoparticles was determined with x-ray powder diffraction (XRD) by a X'Pert Philips Diffractometer using Cu Kα₁ (λ = 1.54056 Å) radiation in the 2θ range of 5–80° and at a scanning rate of 1.5° (2θ)/min. The recorded XRD patterns were compared with JCPDS reference data for phase identification. Field emission scanning electron microscopy (FESEM) was done by a Hitachi S-4160 instrument to investigate the particle size and morphology of the nanoparticles. High resolution transmission electron microscopy (HRTEM) imaging was performed by JEOL JEM-2100 microscope. Brunauer–Emmett–Teller (BET) surface area measurement, hydrogen temperature-programmed reduction (H₂-TPR) and oxygen temperature-programmed desorption (O₂-TPD) tests were carried out using a Quantachrome CHEMBET-3000 apparatus equipped with a TCD detector. BET surface areas were measured at the liquid nitrogen temperature by N₂ adsorption, using the single point method. Prior to the BET measurements, the nanoparticles were evacuated at 400 °C for 3 h under 20 sccm N₂ flow. H₂-TPR experiments were performed on 25 mg of the metal oxides in 10 sccm of 7.0% H₂ in Ar. Prior to reduction, all the metal oxides were treated at 500 °C for 3 h in 10 sccm air

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