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Upgrading of heavy oil by dispersed biogenic magnetite catalysts

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HIGHLIGHTS

- Upgrading by Pd-biomagnetite comparable to commercial alumina supported catalysts.
- Higher liquid yield using Pd-biomagnetite versus alumina based catalysts.
- Significant reduction in coke levels using Pd-biomagnetite.
- Potential for 'green' biosynthesis of Pd-biomagnetite.

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ABSTRACT

In situ catalytic upgrading of heavy oil offers significant cost savings and overcomes logistical challenges associated with the high viscosity, low API gravity and high molecular weight fractions of unconventional hydrocarbon resources. The THAI-CAPRI process (toe-to-heel air injection – catalytic upgrading process in situ) offers one such route to upgrading through the use of high surface area transition metal cracking catalysts surrounding the production well. Here, we describe the catalytic upgrading of heavy oil in a stirred batch reactor by a biogenic nanoscale magnetite (BnM; Fe_3O_4). A 97.8% decrease in viscosity relative to the feed oil was achieved and coking was lower compared to thermal cracking alone (6.9 wt% versus 10.2 wt%). The activity of this catalyst was further enhanced by a simple one-step addition of surface associated Pd to achieve loadings of 4.3, 7.1 and 9.5 wt% Pd. This led to significant decreases in viscosity of up to 99.4% for BnM loaded with 9.5 wt% Pd. An increment of 7.8° in API gravity with respect to the feed oil was achieved for 9.5 wt% Pd-BnM, compared with thermal cracking alone (5.3°). Whilst this level of upgrading was comparable to commercially available and previously tested catalysts, significant decreases in the coke content (3 wt% for 9.5 wt% Pd-BnM versus 10 wt% for thermal cracking) and associated increases in liquid content (~90 wt% for 9.5 wt% Pd-BnM versus ~79 wt% for thermal cracking) demonstrate the potential for the use of Pd-augmented biogenic magnetite as a catalyst in the THAI CAPRI process.

1. Introduction

Continuing depletion of global oil reserves has led to unconventional oil resources, such as oil sands, heavy oil and bitumen becomingly increasingly attractive for exploitation. However, heavy oil and bitumen have the disadvantage of high viscosity, low API (American Petroleum Institute) gravity and high molecular weight fractions. This presents a challenge, as the transportation of these materials is both costly and energetically expensive, with heating of the pipeline or solvent addition often required to improve flow rates [1]. Furthermore, conventional oil refineries require heavy oil and bitumen to be first upgraded to a light crude oil before being distilled [2]. Again, this carries associated costs and hence previous exploitation of these resources has been limited.

This demand for enhanced oil recovery (EOR) has led to the development of in situ upgrading technologies [3]. These present the key advantage that upgrading occurs down-hole, thus, enhancing both production and oil quality whilst precluding the need for a secondary surface upgrading facility. In addition, several environmental benefits are offered as unwanted contaminants or by-products are retained in the reservoir, including heavy metals, sulfur and carbon dioxide [4].

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The THAI-CAPRI process (toe-to-heel air injection; catalytic upgrading process in situ) is one such technique that combines thermally enhanced oil recovery with in situ catalysis of the heavy oil being mobilised [5–7]. First, in situ combustion is advanced by the continuous injection of air through a vertical well (THAI), which allows the combustion front to be sustained. Second, the CAPRI add-on involves the addition of a catalyst to the horizontal production well, which promotes upgrading of the mobilised oil, e.g. via hydrocracking and hydrodesulfurization. However, challenges arise from the use of fixed bed catalysts due to severe deposition of coke, asphaltenes and metals leading to catalyst deactivation [8,9].

Alternatively, dispersed submicron and nano-particulate catalysts may circumvent this by presenting a larger surface area distributed throughout the site of combustion, and hence, overcoming diffusion limitations and pore plugging associated with fixed bed catalysts, which may obstruct production lines [10–12]. Previous work has shown that dispersed micrometer sized Co-Mo/Al_2O_3 showed superior upgrading compared to its millimetre sized pelleted counterpart [10]. Significant upgrading has also been described for dispersed nanoparticulate hematite and several un-supported transition metal nanoparticles, namely MoS_2, NiO and Fe_2O_3 [11,13]. Although the extent of upgrading was modest compared to thermal cracking, these dispersed materials significantly suppressed coke formation, with the remaining coke having a sponge-type character which may find use as an industrial fuel compared with typical coke materials generated from thermal cracking. These studies highlight the potential for the combination of dispersed nano-sized catalysts with the in situ upgrading offered by the CAPRI process, as an alternative to previously used pelleted hydroprocessing catalysts.

Noble metals, such as palladium and platinum also exhibit catalytic upgrading of oil through the promotion of hydrogenation and hydrogenolysis reactions which add hydrogen to the oil molecule (hydrocracking) [14–16]. Supported-Pd catalysts are particularly effective, as the surface area of the palladium is maximised by a nanoparticulate support structure. Typically, this has been done with carbon, silica, alumina and recently bacterial biomass [14,16,17]. Indeed, the use of bacteria in nanocatalyst production represents a more environmentally benign synthesis route.

Further work using bacteria has demonstrated the synthesis of magnetic iron oxide nanoparticles using Fe(III)-reducing bacteria such as *Geobacter sulfurreducens* [18,19]. Biogenic nanoscale magnetite (bionanomagnetite; BnM) has a large surface area, high chemical reactivity and exhibits effective reduction of a range of organics and metals, being notably more efficient at reducing Cr (VI) than a commercially available synthetic Fe_3O_4 [20,21]. Importantly, the particle size of this potential catalyst support can be manipulated during its microbial synthesis, permitting its optimization for novel uses during scalable production [22].

Furthermore, biogenic magnetite is very amenable to surface functionalization with other transition metals such as palladium, mediated by reactive surface Fe(II) and an organic layer facilitating reductive precipitation and attachment of Pd(0) [19]. Pd-biomagnetite is highly reactive toward Cr(VI) and is efficient in hydrogenation of nitroaromatic hydrocarbons and halogenated solvents [21,23,24]. Additionally, when tested in a Heck reaction, coupling iodobenzene to ethyl acrylate or styrene, reaction rates using Pd-biomagnetite were superior or equal to an equimolar amount of commercially available colloidal Pd catalyst [19]. Although Pd is expensive to apply in an oil upgrading process, the cost could potentially be reduced by utilising metal recovered from secondary sources such as electronic waste, scrap catalytic converters or even low grade road dust, which contains traces of platinum group metals exhausted from automotive catalysts [25,26]. In addition, the use of magnetite as a support offers the potential for magnetic recovery and reuse of the catalyst; a major drawback for other precious metal catalyst supports [27].

In light of the previously reported catalytic properties of Pd-bionanomagnetite, and its amenability for optimization for a range of novel uses, this study aimed to assess the catalytic upgrading of oil by biogenic magnetite supported Pd. The upgrading properties of biogenic magnetite alone, as a potential non-functionalised nano-dispersed transition metal catalyst, were also examined. Extents of oil upgrading were assessed in terms of viscosity and API gravity, whilst true boiling point distributions and liquid, gas and coke mass distributions provided important information on oil yields and catalyst efficacy.

2. Material and methods

2.1. Bionanomagnetite (BnM) catalyst preparations

Biogenic magnetite was synthesised by the dissimilatory reduction of Fe(III) in a ferrihydrite suspension, by late-log phase cultures of *Geobacter sulfurreducens* as described previously [19,23,24,28,29].

First, ferrihydrite was synthesised by the rapid hydrolysis of a 0.6 M Fe(III) chloride solution via the dropwise addition of 1 M NaOH to pH 7, whilst stirring vigorously [30]. The resultant precipitate was washed six times by centrifugation at 5000*g* for 20 min, followed by removal of the supernatant and resuspension in 18 MΩ de-ionised water.

A culture of *G. sulfurreducens* was grown in a modified freshwater basal medium containing 20 mM acetate and 40 mM fumarate as electron donor and acceptor respectively [31]. Cultures were grown to late log-early stationary phase at 30 °C under an 80:20 N_2-CO_2 atmosphere [31]. Cells were then harvested by centrifugation at 5000*g* for 20 min and washed three times in sterile 30 mM $NaHCO_3$ at pH 7.

For magnetite production, 1 L of autoclaved medium was prepared containing 20 mM acetate, 100 mM Fe (as ferrihydrite), 30 mM $NaHCO_3$ and 10 μM anthraquinone-2,6-disulfonate (AQDS) as an electron mediator. As before, the medium was sparged with an 80:20 N_2-CO_2 gas mix and adjusted to pH 7. A suspension of the harvested *G. sulfurreducens* culture was added to a final optical density (at 600 nm) of 0.6. The preparation was then incubated at 30 °C for two days in the dark, during which a black magnetic precipitate was produced. This precipitate was then magnetically separated and washed 3 times in 18 MΩ de-ionised water to remove bacterial cells. The production and purity of the magnetite was confirmed by powder X-ray diffraction (XRD) using a Bruker D8 Advance instrument with Cu $K_{\alpha 1}$ radiation. Transmission electron microscopy (TEM) analysis was performed using a Philips microscope equipped with a 200 keV field emission gun and Gatan imaging filter (GIF200). Samples were prepared by suspending in ethanol prior to drop-casting onto holey carbon support films (Agar Scientific).

2.2. Functionalization of biogenic magnetite with palladium

The surface of biogenic magnetite crystallites was functionalized with various wt% Pd loadings (% Pd by mass of BnM) according to methods described previously [19,23]. Precipitation of Pd onto magnetite was achieved via surface Fe(II)-mediated reductive precipitation from a N_2 sparged solution of $Na_2Pd(II)Cl_4$. Bottles containing the magnetite suspended in Pd(II)-containing solutions were agitated on rollers for 12 h in the dark. Excess ions were then removed by washing three times in 18 MΩ de-ionised water under an N_2 atmosphere. Suspensions were then re-suspended in acetone so that the suspensions would be miscible with the oil for reactor