Asphaltene processing with suspended nanocatalyst. Relevance to in situ upgrading

Fenanda Isquierdo, Pedro Pereira-Almao and Carlos E. Scott*

SCHULICH School of Engineering, University of Calgary, 2500 University Drive NW., Calgary, Alberta T2N 1N4, Canada.
* scottc@ucalgary.ca

ABSTRACT

Hot fluid injection(HFI) is a patented process developed at the University of Calgary by a group of researchers at the Schulich School of Engineering that integrates the enhanced recovery and in reservoir catalytic upgrading of bitumen based upon the application of nano-catalytic technology. It is then crucial to understand Asphaltene reactivity (worst fraction of a heavy oil) and conversion pathways utilizing the kind of nano-catalysts used in HFI to improve this new in situ upgrading process.
Pure Asphaltenes were treated under relatively mild conditions. Six catalyst (NiMo, CoMo, NiW, CoW, FeMo and FeW) were prepared using microemulsions. Produce particles were characterized by X-Ray Diffraction (XRD) and the average diameters obtained by Dynamic Light Scattering (DLS). Reaction products were characterized by Microdeasphalting (MDA), Simulated Distillation (SimDist), Micro Carbon (MCR) and Sulfur content. The average particle diameters varied from 342 to 13 nm, with the CoMo and FeMo showing the smallest sizes. Asphaltene conversions were high, thus the CoW, CoMo and NiW produced 62, 61 and 60 % conversion, respectively. For the other catalysts the conversion was between 55 and 58 %. The catalysts also showed good activity and reduction of Sulfur and MCR content as well as the production of lighter hydrocarbons from Asphaltene.

Keywords: In Situ Upgrading, Asphaltenes, Hydroprocessing, Nanoparticles.

1 INTRODUCTION

More than half of the total world oil reserves are heavy oil, extra heavy oil and bitumen, with vast deposits in Canada (Alberta province) and Venezuela (Orinoco region). Due to their low viscosity, high specific gravity, content of heteroatoms and asphaltenes, these heavy materials are more difficult to produce and refine than conventional oils. This has triggered a surge in the research and development of processes to produce and upgrade heavy oils and bitumen[1].

In situ (or downhole) processing has been proposed as a way of producing synthetic oils from heavy oils and bitumen in the reservoir, thus reducing energy demands for field hydroprocessing and decreasing emissions. In a recent report the Society of Petroleum Engineers Research and Development Committee, has recognized the in situ molecular manipulation (in situ upgrading) as one of the major R&D challenges in the petroleum industry.

Hot fluid injection is a patented process [2] developed at the University of Calgary by a group of researchers at the Schulich School of Engineering. It focuses on reducing the environmental footprint of heavy oil production by enhancing the upgrading of bitumen or heavy oil directly in the reservoir. As described in the patent, this technology integrates the enhanced recovery and in reservoir catalytic upgrading of bitumen based upon the application of nanocatalytic technology. It consists of separating the heaviest fraction of the oil at the surface and, using a proprietary device, producing catalytic nanoparticles suspended in the heavy oil fraction which is reinjected in the well. The nanocatalyst is retained in the reservoir and remains active anywhere from several months to a few years. In addition to the granted Canadian Patent, the In Situ Upgrading Technology (ISUT) has been filed for patent protection in the United States, Mexico, Colombia, China, Russia and Brazil. In Situ Upgrading is a paradigm shift that will soon transform the heavy crude oil recovery and upgrading part of the energy business.

Previous publications have shown that in situ upgrading using the hot fluid injection is feasible[3-6]. It is also well known that asphaltenes are the main responsible for coke formation and catalysts deactivation during heavy oil and bitumen processing. A good understanding of asphaltene reactivity and conversion pathways is crucial to better understand and improve this new in situ upgrading process. In the present work the processing of asphaltenes under relatively mild conditions was studied. Different catalytic compositions(NiMo, CoMo, NiW, CoW and FeMo) were tested and the reaction products characterized by Microdeasphalting (MDA), Sulfur content (HDS), Simulated Distillation (SimDist) and Micro Carbon content (MCR).

2 EXPERIMENTAL

2.1 Asphaltenes feedstock preparation

A mixture of asphaltenes and Light Cycle Oil (LCO) was obtained courtesy of CNOOC-NEXEN. The asphaltenes feedstock was extracted from the previous material by the following procedure: , 200 grams of the mixture was poured in to a flask with 4 Lt of n-pentane. The mixture was then heated for 30 minutes at 55 ° C; after cooling, precipitated asphaltenes were recovered by filtration using a Whatman #2 (medium) paper filter and dried in a vacuum oven as previously described [7].

2.2 Catalyst preparation

The particles were prepared using reverse microemulsions, as previously described[8]. In a typical preparation (NiMo) 4 cm^3 of ammonium sulfide (40-48 %wt.) were added to a solution of ammonium heptamolybdate hydrate (0.9180g in 4 cm^3 of water) and the resulting mixture was aged for 5 hours. Then, 5 grams of sodium sulfosuccinate (AOT) were dissolved in 85 g. of deca hydronaphtalene (DHN) at 313 K, with stirring. A microemulsion was formed by adding, drop-wise, the Mo solution to the DHN-surfactant one (maintained at 313 K) with vigorous stirring. The obtained Mo-DHN emulsion was allowed to stand for 15 min and then a nickel nitrate hydrate solution containing 0.664 g. of nickel nitrate in 2 cm^3 of water, was added. The initially orange-red emulsion immediately turned black. The resulting mixture was heated to 338-343 K for 2 hours and finally heated under reflux at 439-443 K for a further 6 h. Particles were separate by centrifugation (6000 rpm for 30 min), washed several times with toluene and vacuum dried at 353 K overnight.

2.3 Hydrocracking of solid asphaltenes

Approximately 1 g of catalyst was dispersed in approximately 20 g of pure asphaltenes and charged in a 100 mL Parr 4590 – Micro Bench Top Reactor. The reactor was closed purge with hydrogen and heated to 380° C (stirring 500 rpm). Once the reaction temperature was reached the pressure was increased to 5.6 MPa and the reactor was maintained at this conditions for 6 hours. After cooling down a sample of gases was withdrawn and the reactor opened. The obtained product was a viscous homogeneous mixture at room temperature. In order to take out the entire product from the reactor a solvent (dichloromethane) was added. A sample before the addition of dichloromethane was saved for further analysis. After addition of the solvent, the mixture (product + dichloromethane) was heated in a rota-evaporator to remove all the solvent and then the product recovered. The catalysts were pre-sulfided before the reaction at 350° C and at 3.5 MPa for 6 hours.

2.4 Product and catalysts characterization

Simulated Distillation of pure asphaltenes and reaction products were performed in an Agilent 6890N gas chromatograph. About 200mg of sample were dissolved in 20 mL of CS_2 and weighted inside a 20mL glass scintillation vials provided with metal caps Samples were then homogenized for 10 minutes in an agitator and transferred to a 2mL auto sampler vials.

For Microdeasphalting analysis about 0.5 grams of samples were weighted in duplicated, a beaker was filled with about 20mL of n-pentane and heating maintained at 55° C around 30 minutes; after it was cool down for 30 minutes, the samples were passed thought a vacuum filtration unit using 0.45µm Millipore membranes.

X-Ray Diffraction patterns, for the solid catalysts, were obtained in a Rigaku X-ray diffractometer with a scanning speed of 0.2 degree/min and a step size of 0.02 degree (2 theta) with Cu Kα radiation, 40 KV and 44 mA. The XRD patterns were referenced to the powder diffraction files (International Centre for Powder Diffraction PDF 2005) using the pattern processing analysis software JADE from Materials Data Inc.

For size determinations the particles were suspended in a base lubricant oil by adding a suspension of the prepared particles in toluene to the base oil in such a proportion as to have approximately 1 10-3 g per liter, and then treating it in a laboratory ultrasonic bath for 1 hour. The size of the particles was obtained by Dynamic Light Scattering (DLS) using a Zetasizer Nano S (Malvern Instruments) equipped with a 4.0 mW He–Ne laser (633 nm) operated at an angle of 173º and a temperature of 298 K to obtain the average particle diameter (Z-Ave) of the suspended particles.

Sulfur content, of the original Asphaltene and reaction products, was determined on an Antek 9000 NS elemental analyzer. The samples were dissolved in toluene and introduce in the analysis chamber by means of an autosampler.

3 RESULTS

XRD patternn for the NiMo, CoWS, and FeMoS cataltys, after sulfiding, show similar characteristics, i.e., broad lines which correspond to MoS_2 or WS_2 with low intensity, indicating low stacking and disorganized packing of the slabs, as previously reported [8]. Also, sharps peaks can be observed, which can be attributed to Ni_9S_8 or Co_9S_8 and FeS (See figure 1). There are also diffraction peaks that indicates the presence of Na_2SO_4, which could be attributed to the surfactant decomposition [8].

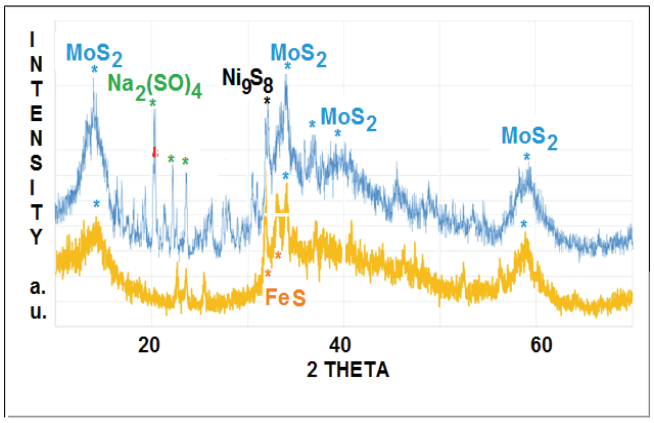

Figure 1. XRD of NiMo and FeMo solids after sulfiding.

DLS results are presented in table 1. The average particle diameters vary from 342 to 13 nm, with the CoMo and FeMo showing the smallest sizes.

Catalyst	Average particle diameter (nm)
FeMo	16
FeW	177
CoMo	13
CoW	117
NiMo	205
NiW	342

Table 1. Average particle diameter for prepared catalysts.

Asphaltene conversions are presented in table 2. It can be observed that all catalysts show very high and similar (55-62 %) conversions.

SimDist was used to get the distribution (by weight) of the different petroleum cuts, namely light naphtha (5-70°C), heavy naphtha (HN; 70-190°C), kerosene (190-250°C), atmospheric gas oil (AGO; 250-350°C), vacuum gas oil (VGO; 350-538°C), and residuum (VR; >538°C), for the original Asphaltene and reactions products. Asphaltene only shows 1.2 and 98.8 wt.% of VGO and VR, respectively. Table 3 presents the distribution of the different cuts in the reactions products obtained with different catalysts. An important increase in the lighter fraction is observed.

Catalyst	Asphaltene conversion (wt. %)
FeMo	55
FeW	58
CoMo	61
CoW	62
NiMo	55
NiW	60

Table 2. Asphaltene conversion for prepared catalysts.

Catalyst	HN/ wt.%	Kero/ wt.%	AGO/ wt. %	VGO/ wt.(%)	VR/ wt.%
FeMo	5.1	6.4	12.4	17.4	58.8
FeW	3.1	7.5	8.4	16.8	64.1
CoMo	2.3	6.4	11.4	19.9	60.1
CoW	2.1	6.4	8.0	16.7	66.8
NiMo	1.8	4.8	10.5	18.5	64.4
NiW	1.7	4.6	11.2	20.1	62.4
Asph	0	0	0	1.2	98.8

Table 3. Distribution of distillation cuts for original Asphaltene and reaction products.

In figure 2 the conversion on the VR fraction (the heaviest fraction of a crude oil) is shown. It can be seen that between 38 to 51 % of that heavy fraction produces lighter material when hydrotreated with the dispersed catalytic particles.

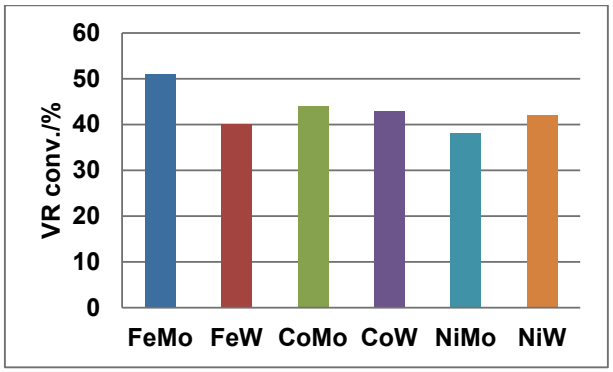

Figure 2. Vacuum residue (VR) fraction conversion obtained with the different catalysts

In figure 3 the micro carbon content for each of the reactions products is observed. Micro carbon content is related to the coke forming tendency of a given petroleum material. This is an important parameter since coke is an undesirable by-product in any upgrading process. The higher the MCR content of a sample the higher the tendency of that sample to form coke. All the reaction products show a decrease in the MCR content. The solids promoted by Co or Ni show the lower values while for the ones promoted by Fe the values are relatively higher. This could be related to the higher cracking tendency previously reported for this metal[9].

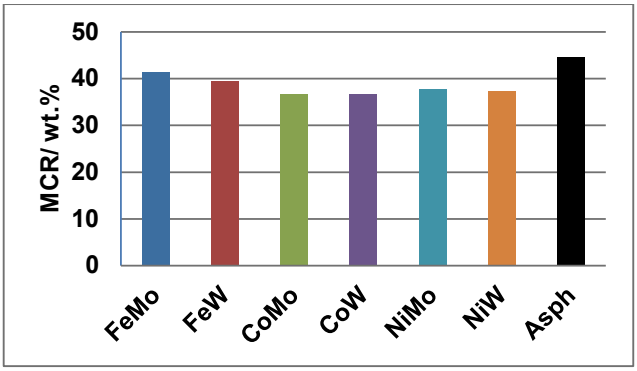

Figure 3. Micro carbon content for the original Asphaltene (Asph) and reactions products obtained with the different catalysts.

It was also found that HDS was between 34 and 47 % for the solids teste as catalysts (see figure 4). The catalysts promoted by Co show higher activity followed by the ones promoted by Ni and last the ones promoted by Fe. This sequence is in agreement with findings reported in the literature that show similar activity correlation for HDS catalysts[10].

Gases were analyzed for every reactions and the composition was fairly similar in all cases the main reactions products being methane, ethane and propane. FeMo catalyst produced more methane (almost double) than the others which

could be related to the higher cracking activity reported for this metal when compared to Ni[9].

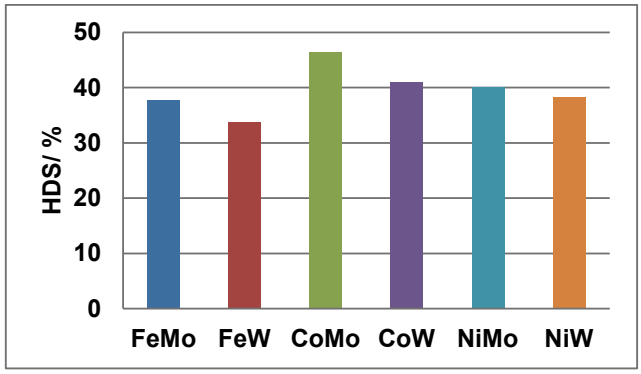

Figure 4 Hydrodesulfurization (HDS) activity obtained with the different catalysts.

In summary it was found that NiMo, CoMo, NiW, CoW, FeMo and FeW catalytic particles (submicrometric to nano sized) can produce high Asphaltene conversion at relatively mild reactions conditions. Asphaltenes (the worst fraction of a heavy oil or Bitumen) can be converted to more valuable products by hydroprocessing it with nano-catalytic particles, like the ones prepared in this work.

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