



# Catalytic cracking of heavy petroleum residue in supercritical water: Study on the effect of different metal oxide nanoparticles



Morteza Golmohammadi<sup>a</sup>, Seyed Javad Ahmadi<sup>b</sup>, Jafar Towfighi<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran

<sup>b</sup> Nuclear Science and Technology Research Institute, Tehran, Iran

## ARTICLE INFO

### Article history:

Received 10 January 2016

Received in revised form 19 March 2016

Accepted 21 March 2016

Available online 22 March 2016

### Keywords:

Vacuum residue cracking

Supercritical water

Nanocatalyst

Catalyst stability

## ABSTRACT

Cracking of heavy petroleum residue obtained from the vacuum distillation unit in supercritical water (SCW) was performed with and without catalysts. First, different nanoparticles, including CeO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and MnO<sub>2</sub> were synthesized in a batchwise SCW reactor; then, the abilities of aforementioned nanocatalysts to convert vacuum residue (VR) into the lighter fractions as well as their stability under severe condition of supercritical water were examined. The X-ray diffractometry (XRD) and transmission electron microscopy (TEM) images indicated that the obtained nanoparticles with a satisfactory size and morphology were synthesized under supercritical condition. VR cracking experiments were also conducted in a batchwise reactor under operating condition, namely temperature: 450 °C, reaction time: 60 min, catalyst/oil ratio (g/g): 1/5, and water/oil ratio (g/g): 80/3. The performance of different nanocatalysts was compared based on the yield of maltene, coke, and asphaltene obtained from VR cracking. As a result, it was determined that the efficiency of nanocatalysts in VR cracking diminishes in the order of CeO<sub>2</sub> > Co<sub>3</sub>O<sub>4</sub> > MnO<sub>2</sub>, while the non-catalytic cracking or SCW pyrolysis attained the lowest rank with a slight difference with the case of MnO<sub>2</sub>. Moreover, the XRD was utilized to investigate the stability of different catalysts. The results demonstrated that only CeO<sub>2</sub> was stable, whereas the other catalysts were reduced to the lower oxidation states during the reaction. Nevertheless, the scanning electron microscopy (SEM) image and the Brunauer–Emmett–Teller (BET) surface area of spent CeO<sub>2</sub> showed the agglomeration of nanoparticles after the reaction.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Over the past decade, the world energy demand has significantly increased; on the other hand, the crude oil reservoirs are decreasing sharply. Thus, such a fast decline in the availability of the conventional oils has caused an essential shift toward the upgrading of heavy oil. Atmospheric and vacuum residues are the two candidates, which could be transformed into valuable light fuels [1]. The latter residue is the heaviest fraction achieved from the bottom of the vacuum distillation column tower at the end of fractional distillation. It is characterized by high density, viscosity and molecular weight, large amounts of asphaltenes, large contents of heteroatoms such as sulfur, nitrogen and oxygen compounds, as well as heavy metals including vanadium, nickel, chromium, iron, etc. but low atomic hydrogen to carbon ratio [1,2]. Thermal cracking, catalytic cracking, and hydrocracking are the common

processes for upgrading of heavy oils. However, coke formation during the cracking is a major obstacle in these operations, which deactivates the catalyst and reduces the upgrading efficiency. Although the use of hydrogen gas in the hydrocracking can lessen the coke formation, hydrogen production costs make this process considerably expensive. Upgrading of heavy oils in supercritical water (SCW) medium is a comparatively new approach receiving attentions because of its advantages. SCW can dissolve light hydrocarbon due to drastic decrease of water dielectric constant around the supercritical point, which leads to better miscibility between water and heavy oil [3]. Water disperses the coke precursors formed from oil cracking and therefore the quantity of coke decreases by means of SCW [3,4]. Furthermore, SCW is capable to form in-situ hydrogen through hydrocarbons reforming, and/or partial oxidation of hydrocarbons followed by water gas shift reaction [5–7]. In this reaction, the hydrocarbons reforming/oxidative cracking takes place to form CO. Then the formed CO experiences the water gas shift reaction (WGS) with SCW to produce in-situ hydrogen and consequently the hydrogenation of hydrocarbon occurs. Also, Hosseipour et al. [8] proposed that the water dissociation on the surface

\* Corresponding author.

E-mail address: [Towfighi@modares.ac.ir](mailto:Towfighi@modares.ac.ir) (J. Towfighi).

of a catalyst, in the case of SCW catalytic cracking, is another source for the creation of in-situ hydrogen. It is reported that this kind of hydrogen is more active than molecular hydrogen for hydrogenation of heavy oils in sub and supercritical water [9,10]. The oxygen required for oxidative cracking, CO production, and finally the formation of in-situ hydrogen can be supplied by air [11], hydrogen peroxide [12], or lattice oxygen of the catalyst in the case of catalytic cracking [8]. Moreover, CO-supporter agents such as formic acid are used in such a way that they can decompose to form CO followed by active hydrogen generation through WGS [13,14].

Several research works have been conducted to study the upgrading of heavy oils e.g. bitumen, vacuum residue (VR), sand oil, etc. in SCW. Zhao et al. [15] investigated the effect of temperature, pressure, and reaction time on product distribution. Based on their results, the content of saturates in the liquid product increased, while the contents of aromatics, resins, and asphaltene decreased with temperature. Moreover, they noted that the reaction time should be considered as an important factor in coke generation, whereas pressure showed no significant effect on coke formation. Sato et al. [13] examined the upgrading of bitumen with formic acid in SCW at different temperatures and water/oil ratios. They claimed that decomposition of asphaltene was promoted and coke formation was suppressed using the combination of SCW+ HCOOH because formic acid produces active species in SCW. Although non-catalytic upgrading of the heavy oils in SCW have been studied extensively, a limited domain of research has been allocated to the catalytic cracking of heavy oils in SCW. Fedyaeva et al. [16] studied the cracking of bitumen in the presence of zinc and aluminum in SCW. They reported that the hydrogenation of bitumen was significantly increased due to hydrogen formation during oxidation of the metals in SCW. Dejhosseini et al. [17] investigated the catalytic cracking of bitumen with cerium oxide nanoparticles in SCW. They synthesized two kinds of CeO<sub>2</sub> with different morphologies, namely octahedral and cubic ones and found that the highest conversion of asphaltene could be achieved in the presence of the cubic CeO<sub>2</sub>. Recently, Hosseinpour et al. [12] applied Fe<sub>2</sub>O<sub>3</sub> nano-powder and silica supported Fe<sub>2</sub>O<sub>3</sub> in SCW cracking of VR. Besides, they employed isotope labeling technique using deuterium oxide (D<sub>2</sub>O) as well as ATR spectroscopy in order to elucidate the role of water in SCW cracking of VR. Accordingly, they concluded that water in supercritical state takes part in the reaction of in-situ hydrogen generation, because a substantial H-D exchange was observed in the ATR pattern of liquid products after treatment in supercritical deuterium oxide.

Nanomaterials provide a large surface area that is supposed to pave the way for an appropriate activity for a wide variety of reactions. There are various methods to synthesize nanoparticles, including sol-gel, chemical vapor deposition, hydrothermal methods, ultrasonic irradiation, and hydrothermal synthesis using SCW. Among aforementioned techniques, the SCW has been exploited extensively in the last two decades [18]. This method is environmentally friendly because no organic solvents are used during the process. Moreover, the high reaction rate, the obtained small particle size, and the tuning ability of the process that is a result of the drastic change in the physical properties of water in the vicinity of its critical point are the main advantages of this method compared to the other techniques [19]. Numerous works have aimed at synthesizing of a wide range of metal oxide nanoparticles utilizing SCW for different purposes [20–25]. Application of nano-scale catalysts, nanocatalysts, for upgrading of heavy oils in SCW, as far as we are concerned, is an interesting research field. Nonetheless, the nanocatalysts must be stable in severe condition of SCW and possess an acceptable activity for cracking of heavy oils. To the best of our knowledge, the metal oxides with a worthwhile activity for asphaltene adsorption/oxidation as well as high oxygen storage/release capacity are good candidates for SCW VR

**Table 1**  
Properties of feedstock in addition to elemental analysis.

M <sub>w</sub> (mol/g)	ρ <sub>4</sub> <sup>20</sup> (g/cm <sup>3</sup> )	ν <sup>80</sup> (mm <sup>2</sup> /s)	Elemental analysis (wt%)				
			C	H	S	N	H/C (mol)
1860	1.006	2550	84.79	10.42	3.5	1.112	1.475

upgrading. Nassar et al. [26] examined the activity of some transition metal oxides, including Fe<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, and NiO for asphaltene adsorption/oxidation. They found that this activity decreases in the order of NiO > Co<sub>3</sub>O<sub>4</sub> > Fe<sub>3</sub>O<sub>4</sub>. Moreover, Daud [27] studied the partial oxidative cracking of phenanthrene as a model compound of asphaltene. They investigated the phenanthrene cracking in the presence of air, as oxidant, MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> catalysts. Their results indicated that phenanthrene-air-MnO<sub>2</sub> system showed the highest phenanthrene conversion and oxygenated intermediates yield.

Cerium dioxide, commonly known as ceria, is well-known because of its high oxygen storage capacity (OSC) [28–31]. This property of CeO<sub>2</sub> is very beneficial for oxidative catalytic reactions in such a way that the ceria can release its surface and lattice oxygen to reaction medium. However, the reversible redox reaction of Ce<sup>3+</sup>/Ce<sup>4+</sup> is very necessary to preserve the catalytic activity. According to the literature [12,17,32], in SCW condition, both hydrogen and oxygen species can be generated from the splitting of water over the catalyst; the latter can be adsorbed on the catalyst surface to complete the redox cycle. This property of SCW along with the easy conversion between Ce<sup>3+</sup>/Ce<sup>4+</sup> makes the ceria as an appropriate catalyst for VR cracking in SCW.

In the current study, different nanoparticles, including CeO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and MnO<sub>2</sub> are synthesized by the SCW technique, and their textural, and structural properties are characterized. Then the performance of these catalysts in upgrading of VR was investigated from the reaction yield as well as the catalytic stability point of view.

## 2. Experimental methods

### 2.1. Materials

Cerium (III) nitrate hexahydrate, cobalt (II) nitrate hexahydrate, and manganese (II) nitrate hexahydrate (all high purity salts from Merck) were employed as an initial source for catalyst synthesis. The vacuum residue (VR) was provided from the bottom of the vacuum distillation unit of Tehran Refinery Company with specified properties shown in Table 1. Carbon, hydrogen, and nitrogen (CHN) contents of the feedstock were measured by the elemental analysis instrument (Elementar vario EL III, Germany). The solvents utilized in the preparation of feedstock, precipitation and extraction of VR fractions were chloroform (99%), toluene (99%) and *n*-hexane (99.6%), all obtained from Merck.

### 2.2. Nanoparticles synthesis and characterization

The aqueous feed solutions were prepared by dissolving the metal nitrate salts in distilled water so that the concentration of metal nitrate solution was adjusted to about 0.1 M. The synthesis of metal oxide nanoparticles was accomplished by supercritical water treatment of the metal nitrate salts in a stainless steel (type 316L) autoclave with a capacity of 200 cm<sup>3</sup>. In order to preserve adequate safety margin, the reactor was loaded with only one third of its volume and was then placed in a furnace adjusted at the temperature of 500 °C and kept for 2 h. Thereafter, the reactor was removed from the furnace, submerged in cold water, and the precipitated nanoparticles were separated from the solution by applying a high speed centrifugation (12,000 rpm, 15 min). After centrifugation, the

Download English Version:

<https://daneshyari.com/en/article/230001>

Download Persian Version:

<https://daneshyari.com/article/230001>

[Daneshyari.com](https://daneshyari.com)