



# On the catalysis capability of transition metal oxide nanoparticles in upgrading of heavy petroleum residue by supercritical water



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## ARTICLE INFO

### Article history:

Received 28 November 2016

Received in revised form 24 February 2017

Accepted 24 February 2017

Available online 27 February 2017

### Keywords:

Catalytic cracking

Supercritical water

Metal oxides nanocatalysts

Oil residue upgrading

## ABSTRACT

Vacuum residue cracking has been successfully conducted under supercritical water condition in presence of various metal oxide nanocatalysts, namely NiO, CuO, ZnO, Co<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> synthesized at supercritical water. The cracking experiments were carried out at 450 °C. Three species of cracking: maltene, asphaltene, and coke were then weighed and their corresponding speciation was defined. Gas chromatography-mass spectrometry (GC-MS), nuclear magnetic resonance spectroscopy (NMR), thermogravimetric analysis (TGA), and elemental analysis (CHNS) tests were utilized to prove the performance of upgrading reactions. It was revealed that NiO showed the best performance among other catalyst, in which its activity and stability in catalytic cracking changed slightly. According to the results obtained from GC-MS, NMR, TGA, and CHNS analyses, it was confirmed that the proportion of heavy hydrocarbons of products (i.e. non-catalytic and catalytic reactions) was lower than that of feedstock.

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## 1. Introduction

Demand for energy is growing up enormously, consequently, man faces the drastic depletion of crude oil resources causes that the petroleum residues, heavy oils and bitumens are going to increase more and more. Needs to find a way to reuse the oil residual as crude oil's alternative has initiated new techniques to upgrade heavy oil components.

To pave the way for benefiting from the usable compositions and for being able to convert them to light components, atmospheric and vacuum residues (AR & VR) have found significant applications for producing valuable light hydrocarbon components through different research projects. Specifications of VR, the heaviest fraction produced from the bottom of the vacuum distillation column tower, include high viscosity, molecular weight and density, large proportion 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].

Most of the scientists who worked on the upgrading of heavy oil and even bio-oil, exploited many technical approaches and various catalytic agents and chemical reagents. According to the literature, indeed, many reporters investigated the design of various systems and experiments for cracking of the heavy oil components have unanimously mentioned that high temperature is a key factor for a desired transformation. The related data for cracking and heavy oil upgrading, so far, numerous methods have been investigated, among which hydro-thermal cracking, thermal cracking and catalytic cracking have been much more appealing to many [2–6]. All of these methods suffer from a major issue named coke formation, an unwanted product in a cycle of procedures. Coke is regarded as a catalytic poison and declines the upgrading efficiency. Nevertheless, it is found that the presence of H<sub>2</sub> during hydro-thermal cracking can obviate the coke formation to some extent.

Recently, supercritical water (SCW) utilization along with other methods has been investigated during cracking of heavy petroleum residue. As temperature arises higher than critical point (374 °C and 22.1 MPa), water dielectric constant ( $\epsilon$ ) declines drastically giving SCW, an excellence feature to dissolve the organic components easily and to cause better miscibility between water and heavy oil [1]. Another property of SCW is the dispersion effect in which heavy organic molecules can be repelled from each other dur-

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ing the treatment process in SCW medium [7]. This property can lead to the decomposition of heavier components such as bitumen and production of lighter compounds, which are prevented from recombination. Partially dissolution and dispersion of asphaltene as an emulsion could happens while it is in SCW; this phenomenon declines the asphaltene concentration for coking and slowing down the coking reaction due to the existence of the mass-transfer resistance between different emulsion droplets [7]. Thus, SCW could disperse the formed coke precursors and consequently the amount of coke declines considerably [7,8]. Another subtle point about SCW here is that it is capable of producing in-situ hydrogen through hydrocarbons reforming, and/or partial oxidation of hydrocarbons led from water gas shift reactions (WGSR) [9–11]. It is reported that during catalytic cracking of the oil components using SCW, as water is dissociated on the surface of the catalyst, a sort of active hydrogen, which differs from that of molecular forms, for hydrogenation of heavy oils in sub and supercritical water, is produced [11–13]. Some ways such as using hydrogen peroxide [14] and engaging lattice oxygen of the catalyst in the case of using a catalyst [12] can be followed to supply the required oxygen for oxidative cracking, CO production, and the formation of in-situ hydrogen. Furthermore, there is another method in which CO-supporter agents such as formic acid can decompose to form CO followed by active hydrogen generation through WGSR [15,16].

Cracking of the heavy petroleum residue e.g. bitumen, vacuum residue (VR), sand oil, crude bio-oil, etc. in SCW, near-CW, and sub-CW with and without catalyst has been investigated through a number of research works [17,18]. Most of them have focused on interpretation of cracking phenomenon under sub- and supercritical conditions, trying to discover the actual mechanism through the upgrading process. However, a great deal of researches has been allocated to the non-catalytic upgrading of heavy oil. Consequently, reports on catalytic cracking in this domain are quite scarce. For instance, Golmohammadi et al. synthesized cerium oxide (CeO<sub>2</sub>), cobalt oxide (Co<sub>3</sub>O<sub>4</sub>), and manganese oxide (MnO<sub>2</sub>) and applied those catalysts in upgrading of VR [1]. They found that cerium oxide, because of its large oxygen storage capacity, can share oxygen with heavy hydrocarbons in the oxidation process under supercritical condition. Furthermore, there are some other reports on the use of different nanoparticles including MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO, Co<sub>3</sub>O<sub>4</sub>, and CeO<sub>2</sub> in heavy oils upgrading [14,19–21].

Nano-structured metal oxides have recently found a particular position in chemical industry, supramolecular chemistry, green chemistry, catalytic cracking and so forth [22–24]. These materials tend to offer a larger surface area, higher amounts of accessible active sites as well as facile diffusion of reactants and products, therefore, they could lead to significantly enhanced catalytic activity. For synthesizing super-fine and nanometric particles, numerous researches have been conducted, among them SCW has been successful in production of a wide range of metal oxides with desirable features including smaller size, uniform shape, and large surface area [25–29]. SCW is also known as a benign and environmentally friendly method in which no organic solvents are used in the process. Great deals of researches have followed the application of nano-structured catalysts for heavy oil upgrading in SCW.

To the best of our knowledge, transition metal oxide nanoparticles with a striking activity for asphaltene oxidation/adsorption as well as high oxygen storage/release capacity are the most utilized nanocatalysts in the domain of SCW VR cracking. Oxidation of asphaltene was performed using six nanoparticles (CuO, Co<sub>3</sub>O<sub>4</sub>, NiO, Mn<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) through an enhanced oil recovery (EOR) technique, reported in Ref. [30]. It was reported that Co<sub>3</sub>O<sub>4</sub>, NiO, and Mn<sub>2</sub>O<sub>3</sub> are the powerful metal oxides in their redox capability. Another investigation was dedicated to evaluation of the thermodynamics of asphaltene adsorption on metal oxide nanoparticles with acidic and basic surfaces [31]. Metal oxides/salts nanoparticles

**Table 1**

Properties of feedstock in addition to elemental analysis (provided by Tehran Refinery Company).

Mw (g/mol)	$\rho_4^{20}$ (g/cm <sup>3</sup> )	$\nu^{80}$ (mm <sup>2</sup> /s)	Elemental analysis (wt%)				H/C
			C	H	S	N	
1860	1.006	2550	84.79	10.42	3.50	1.11	1.48

including NiO, WO<sub>3</sub>, MgO, CaCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> were used in this research work. It was found that asphaltene adsorption capacity was higher for NiO and Fe<sub>2</sub>O<sub>3</sub>. As well as two above mentioned procedures, another research reported using of Fe<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>, MgO, CaO, and NiO, which showed the feasibility of using nanoparticles for asphaltene adsorption, followed by catalytic oxidation for heavy oil upgrading [32]. Nevertheless, there is no a general report on the catalytic effect of nanostructured metal oxides on the cracking of heavy oil in SCW. Based on abovementioned studies, the use of metal oxide nanoparticles for upgrading of heavy oil in supercritical condition would be practical due to their abilities to attend in the redox cycle.

Herein, we firstly exploited SCW technique for synthesizing different transition metal oxide nanoparticles including NiO, CuO, ZnO, Co<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>. Afterwards, the morphology, textural, and physicochemical properties of nanoparticles were characterized by means of various techniques. Subsequently, we benefited from SCW and the synthesized nanoparticles in a non-catalytic and catalytic cracking process for upgrading of VR. Finally, the upgrading performance was assessed by using various techniques including gas chromatography-mass spectrometry (GC-MS), nuclear magnetic resonance spectroscopy (NMR), thermogravimetric analysis (TGA), and elemental analysis (CHNS).

## 2. Experimental

### 2.1. Materials

Highly pure zinc (II) nitrate hexahydrate, copper (II) nitrate trihydrate, nickel (II) nitrate hexahydrate, chromium (III) nitrate nonahydrate, and cobalt (II) nitrate hexahydrate used as precursors for catalyst synthesis in supercritical water were purchased from Merck. N-hexane 99%, toluene, and chloroform used as solvents after cracking reaction for speciation of maltene, asphaltene and coke were prepared from Sigma-Aldrich. A stock of vacuum residue provided from the bottom of the vacuum distillation column of Tehran Refinery Company was utilized for cracking tests, which its properties provided by Tehran Refinery Company and are listed in Table 1.  $\rho_4^{20}$  indicates the density of feed stock (VR) at 20 °C,  $\nu^{80}$  stands for kinematic viscosity of VR at 20 °C, and  $M_w$  is molecular weight.

### 2.2. Instruments

X-ray diffraction (XRD) analysis was conducted by a Philips X'pert powder with Cu-K $\alpha$  ( $\lambda = 1.541 \text{ \AA}$ ), to study the crystal structure and composition of the samples. Fourier transform infrared spectroscopy (FTIR) of the metal oxide nanoparticles was recorded using standard KBR disc technique in the range of 4000–400 cm<sup>-1</sup> by a Bruker FTIR model-Vector22. Temperature-programmed hydrogen reduction (H<sub>2</sub>-TPR) was employed to study catalyst reducibility. H<sub>2</sub>-TPR experiments were carried out in a conventional flow apparatus (NanoSORD NS91) equipped with a thermal conductivity detector (TCD). A 0.03 g of the catalyst placed in a U-shaped quartz microreactor, was pretreated in a flow of 0.6 l/h Ar at 300 °C for 1 h, and cooled down to room temperature in the same atmosphere. The reducing gas, a mixture of 5 vol% H<sub>2</sub> in

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