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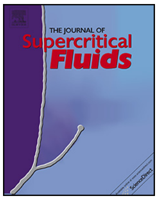

Successive co-operation of supercritical water and silica-supported iron oxide nanoparticles in upgrading of heavy petroleum residue: Suppression of coke deposition over catalyst

Morteza Hosseinpour [a], Seyed Javad Ahmadi [b], Shohreh Fatemi [a,*]

[a] School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran
[b] Nuclear Science and Technology Research Institute, End of North Karegar Ave., Tehran, Iran

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ABSTRACT

The chemical effect of supercritical water (SC-H_2O) on catalytic cracking of heavy petroleum residue was investigated over silica-supported hematite iron oxide nanoparticles, and the stability of catalyst against coke formation was approved by numerous analyses after sequence of reactions. First, the catalysts of process, with different active phase (α-Fe_2O_3) to support (SiO_2) weight ratio, were prepared successfully via supercritical water impregnation approach. The performance of the α-Fe_2O_3–SiO_2 was then considered on transformation of vacuum residue (VR) to lighter fuels in supercritical water medium. Comparing the results with non-catalytic degradation, i.e., SC-H_2O pyrolysis, improvement of heavy oil conversion towards lighter fragments (maltene) was attained. The higher amount of asphaltene transformation as well as suppression in coke formation over/in catalyst could be attributed to larger portion of cracking occurred mainly in catalyst surface and pore volume (PV), whereas the cracking based on pyrolysis was accomplished free-radically in bulk volume (BV). In catalytic reaction, a consecutive cyclic reaction is taking place as; oxidative cracking of asphaltene over catalyst (with converting $Fe^{3+} \rightarrow Fe^{2+}$) followed by in-situ hydrogenation of cracked fragments via in-situ hydrogen resulted from dissociation of water (with converting $Fe^{2+} \rightarrow Fe^{3+}$). Moreover, SC-$H_2O$ reforming of hydrocarbons (C_mH_n) and conversion of those containing oxygen-containing groups, e.g., ethers, esters, carboxyls, carbonyls, to CO as well as related water–gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) would facilitate over catalyst by which higher amount of asphaltene conversion and maltene yield were attained.

1. Introduction

Due to the declining reservoirs of crude oil and environmental concerns, it is necessary that greater amount of petroleum residue be converted to light fractions. Moreover, growing demand for conventional light petroleum products has prompted the petroleum industry to refine heavier crude oils of lower quality [1]. Vacuum residue (VR) is the heaviest fraction of petroleum refinery processes, which is obtained from the bottom of the vacuum distillation column tower. It is categorized by a high molecular weight, low atomic hydrogen to carbon ratio (H/C ratio), high density, and particularly high viscosity. Also, VR comprises higher concentrations of heteroatoms, i.e., sulfur, nitrogen, and oxygen compounds and heavy metals such as vanadium, nickel, and iron [1,2]. Coke formation is the most difficult challenge encountered during residue conversion which deactivates solid catalyst [3,4].

Several strategies have been suggested to upgrade heavy petroleum residue and bitumen into lighter fractions with fewer contaminants including hydrogen addition processes [5] and solvent deasphalting [6]. Recently, study around in-situ hydrogenation of VR in supercritical water (SC-H_2O) [7,8] has been received various attention due to its properties, such as low viscosity, low dielectric constant and high density at rather high temperatures. At $T > 374\,^{\circ}C$ and $P > 22.1$ MPa, water becomes an effective solvent with good miscibility with heavy organic substances and gases [9–13]. There are numerous advantages of upgrading heavy oils in SC-H_2O: dielectric constant and Honsen solubility parameters, i.e., dispersive, polar, and hydrogen bonding which are noticeable for ordinary water. These properties make water as a poor hydrocarbon solvent while they drastically decrease around the critical point and enhance miscibility of water with heavy oil [11]. These excellent salvation and dispersion properties strongly influence on degree of

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* Corresponding author. Tel.:+98 21 61112229; fax: +98 2166957784.
E-mail address: shfatemi@ut.ac.ir (S. Fatemi).

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cracking and suppression of polymerization reaction. Furthermore, compared to external hydrogen addition processes, such as hydrocracking and hydrotreating, in-situ hydrogenation occurs through water gas shift reaction (WGS: $CO + H_2O \rightarrow H_2 + CO_2$), collaborate with carbon monoxide supplier entrainers (oxygen, formic acid, etc.) [14–18], which create more active hydrogen than molecular hydrogen. For such a hydrogenation, however, continuous co-feeding of mentioned entrainers seems indispensable.

In spite of the extensive studies around the above-sited non-catalytic upgrading in SC-H_2O media, a little effort has been devoted to the catalytic treatments of heavy oils in high temperature water. Generally, the aforementioned studies [19–31], which are summarized in Table 1, aimed at developing new routs of catalytic treatment of heavy oil with chemical collaboration of high temperature water. In a case of reaction over heterogeneous catalyst, limited mass transfer caused from poor diffusion in catalyst pores are enhanced through modification in SC-H_2O transport properties (interfacial tension, viscosity, heat capacity, diffusion coefficient, and density). Consequently, capillary forces in catalyst pores decrease significantly and the modified effective diffusion leads to enhancement in the catalytic conversion and prevention of coke formation on catalyst [13]. As an important case, catalytic cracking of petroleum residue with iron oxide catalyst was conducted in high temperature steam in which larger amount of lighter fuels, such as gasoline, kerosene, and gas oil without any coke was concluded [19–21]. In these studies, although the formation of coke was inhibited significantly, however, phase transformation of catalyst (hematite to magnetite) was happened through heavy oil reaction with lattice oxygen in the iron oxide in which deactivation of catalyst was deduced.

In this work the catalytic cracking of heavy petroleum vacuum residue over silica-supported iron oxide granules, as a prominent catalyst of WGS reaction [32–34], was investigated in SC-H_2O with the focus on the study of coke formation over/in catalyst. Based on the experimental results of spent catalyst and comparison of maltene yield, asphaltene conversion and coke yield in the presence and absence of catalyst, the possible pathway of the SC-H_2O hydrogen-donation responsible for the higher amount of maltene with suppression in coke formation in catalytic cracking was proposed.

2. Experiment and methods

2.1. Catalyst preparation

$Fe(NO_3)_3 \cdot 9H_2O$ (Merck AG. Fur synthesis) was prepared as the precursor in this study. Impregnation of iron oxide nanoparticles on silica-support was performed in a stainless steel batch reactor, which was planned especially to endure working temperature and pressure up to 550 °C and 610 atm, respectively. The capacity of the reactor was 200 cm^3, but it filled up to one third of its volume with a 0.1 mol dm^{-3} $Fe(NO_3)_3$ solution with about 2 g of highly porous silica ($SA_{BET} = 500\ m^2/g$). The silica support was allowed to soak in the precursor solution at ambient temperature for time 30 days recommended by other researchers [35,36]. Temperature inside of autoclave was sensed with a high precision thermocouple, however, design of autoclave did not allow to modify for measuring the inside pressure of reactor during experiments. Hence, the inside pressure was calculated from water densities at each temperature using steam tables (approximately in the range of 400–420 atm). The reactor was then heated at 500 °C for about 60 min. This operational condition was selected from our previous studies on the synthesis of metal oxide nanoparticles in SC-H_2O [37,38]. Afterward, it was removed from furnace and quenched by cold water. The iron oxide deposited on silica particles, namely S_1, was separated from the rest of suspended nanoparticles in solution by decantation, and underwent a triple washing-decantation procedure by distilled water. Subsequently, they were spread on some Petri dishes and dried at ambient condition. High speeds centrifuging procedure was applied to separate and wash the suspended particles remained in solution. Drying of iron oxide powders was accomplished in similar manner as mentioned for supported case.

Fig. 1. Low and high iron oxide to silica support weight ratio: S_1 $\left(\frac{150\,\text{mg}\ \ Fe_2O_3}{\text{g}\ \ \text{support}}\right)$ and S_2 $\left(\frac{12\,\text{mg}\ \ Fe_2O_3}{\text{g}\ \ \text{support}}\right)$ was achieved by manipulating in the amount of silica support.

Similar procedure was performed for the synthesis of diluted iron oxide impregnated over/in silica-support, i.e., S_2. For this case, the amount of support introduced to the autoclave was increased continually until the required amount of deposition was achieved. The amount of α-Fe_2O_3 deposited over silica support estimated by inductively coupled plasma–optical emission spectroscopy (ICP–EOS) found to be approximately 0.15 and 0.012 g (α-Fe_2O_3/g silica support) for S_1 and S_2 sample, respectively (see Fig. 1).

2.2. Upgrading and product analysis procedure

Toluene (99%), *n*-hexane (99.6%) and chloroform (99%), were purchased from Merck Chemical Company. The employed VR, in this work, was prepared from bottom of the vacuum distillation unit (Tehran Refinery Company). Its analysis is as follows: API gravity at 20 °C = 9.16, molecular weight = 1860 g/mol, kinematic viscosity at 80 °C = 2550 mm^2/s, water ≤ 1 w/w%, H/C wt ratio = 1.475, sulphur = 3.5 w/w%, nitrogen = 1.112 w/w%. According to the main procedure was used for the subsequent product analyzing, maltene and asphaltene of feedstock were found to be 79 and 21 wt.%, respectively. Here, maltene is defined as the *n*-hexane soluble component including saturates, aromatics, hard and soft resins fractions, whereas asphaltene is *n*-hexane insoluble or toluene soluble fraction.

Upgrading of VR was carried out in a 316-stainless steel batch micro-reactor (10 ml in volume) with a high temperature control precision (±2 °C). For all runs, the temperature was selected at 450 °C. Although thermodynamic studies accomplished on phase behavior of heavy oil + water are limited up to the critical temperature of water [39,40], however, the optimum temperature, of 450 °C was recommended by numerous researchers in order to gain higher amount of light product, asphaltene conversion with suppression in coke formation [7,11,14,22]. Furthermore, the effect of temperature on the level of miscibility of heavy oil in SC-H_2O was observed visually [41] which demonstrate a single phase with complete miscibility in 450 °C. Through the limitations in design of autoclave, measuring the inside pressure of reactor was impossible and was