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

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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_2 , Co_3O_4 , and MnO_2 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 $\text{CeO}_2 > \text{Co}_3\text{O}_4 > \text{MnO}_2$, while the non-catalytic cracking or SCW pyrolysis attained the lowest rank with a slight difference with the case of MnO_2 . Moreover, the XRD was utilized to

investigate the stability of different catalysts. The results demonstrated that only CeO_2 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_2 showed the agglomeration of nanoparticles after the reaction.

Key words: Vacuum residue cracking, Supercritical water, Nanocatalyst, Catalyst stability

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 (WGSR) 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 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 WGSR [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 CeO₂ 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 CeO₂. Recently, Hosseinpour et al. [12] applied Fe₂O₃ nano-powder and silica supported Fe₂O₃ in SCW cracking of VR. Besides, they employed isotope labeling technique using deuterium oxide (D₂O) 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 upgrading. Nassar et al. [26] examined the activity of some transition metal oxides, including Fe_3O_4 , Co_3O_4 , and NiO for asphaltene adsorption/oxidation. They found that this activity decreases in the order of $\text{NiO} > \text{Co}_3\text{O}_4 > \text{Fe}_3\text{O}_4$. Moreover, Daud et al. [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_2 and Fe_2O_3 catalysts. Their results indicated that phenanthrene-air- MnO_2 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_2 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 $\text{Ce}^{3+}/\text{Ce}^{4+}$ 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 $\text{Ce}^{3+}/\text{Ce}^{4+}$ makes the ceria as an appropriate catalyst for VR cracking in SCW.

In the current study, different nanoparticles, including CeO_2 , Co_3O_4 , and MnO_2 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 316 L) autoclave with a capacity of 200 cm³. 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 (12000 rpm, 15 min). After centrifugation, the nanoparticles were collected at the bottom of the centrifuge tube so that the supernatant could be easily removed by decanting it. In order to remove any impurity, enough amount of distilled water was poured into the tube and precipitated nanoparticles were dispersed using a micro spatula and shaking the centrifuge tube. These steps were repeated two times and finally the obtained nanoparticles were transferred to Petri dishes to be dried at the ambient temperature. It should be noted that measuring the inner pressure of the reactor was impossible because of the limitations in design of the autoclave. Therefore, the corresponding pressure was calculated from the steam tables ($T=500\text{ }^{\circ}\text{C}$, $v=0.002952\text{ m}^3/\text{Kg}$, $P=60\text{ Mpa}$).

The crystal structure and composition of the nanoparticles were analyzed by X-ray diffractometry (XRD, Philips PW 1800) with the Cu-K α radiation line. Fourier-transform infrared spectroscopy (FTIR) spectra of the nanoparticles were recorded on a Thermo Nicolet Smart Golden Gate MKII single reflection ATR spectrometer from 400 to 4000 cm^{-1} . The size and morphology of the obtained nanoparticles were characterized by transmission electron microscopy (TEM, LEO 912AB).

Moreover, the scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area measurement as well as temperature-programmed hydrogen reduction (H_2 -TPR) were employed in order to investigate the catalytic performance of CeO_2 nanoparticles during the sequential cracking experiments. For SEM, nanoparticles were firstly dispersed in ethanol by water bath sonication for 15 min. The samples were dropped onto a clean surface, allowed to dry and afterwards mounted on the SEM stubs with carbon adhesive tabs. The nanoparticles were

then coated with a thin layer (20 nm) of gold and observed in the microscope of a KYKY SEM-EM3200 apparatus conducted in the vacuum mode, at an acceleration voltage of 26 kV and magnification of 40000 $\times$. BET surface area of CeO₂ was measured volumetrically by N₂ adsorption using single-point method (Quantachrome instruments, Nova-2000e). The samples were degassed at 150 °C, and N₂ adsorption were performed at 77.3 K in which the temperature was maintained constant by using liquid nitrogen. H₂-TPR was carried out in a conventional flow apparatus (NanoSORD NS91). A 0.03 g of the catalyst placed in a U-shaped quartz microreactor, was pretreated in a flow of 10 sccm Ar at 300 °C for 1 h, and cooled down to room temperature in the same atmosphere. The sample was then reduced in the H₂ (5.0%)/Ar flow (10 sccm) while the temperature was raised to 950 °C at a constant heating rate of 10 °C/min. The amount of consumed H₂ was detected by means of an online thermal conductivity detector (TCD).

The total oxygen storage capacity (OSC) of a material is generally defined as the total amount of O₂ that may be extracted from it at a pre-established temperature and partial pressure of reducing agent such as H₂, CO, etc. In this study the total OSCs for the catalysts were determined based on H₂-TPR tests, in which the total integrated area under the H₂-TPR curve corresponds to the H₂ consumption during the reduction of catalyst. Moreover, the volume of hydrogen consumed by the samples was calibrated against the reduction of Ag₂O under similar conditions of the TPR experiments. Eventually, the amount of consumed O₂, and consequently the total OSC can be calculated based on Eq. (1):

2.3. Cracking of vacuum residue

In order to remove any probable impurity such as coke, ash, etc. accumulated during the crude oil refining process, the feedstock was centrifuged after dissolving in the chloroform. After

evaporation of the solvent, the composition of the feedstock was measured by applying solvent extraction procedure based on the standard method of ASTM D6560-00 as shown in Fig. 1. Accordingly, it was determined that the feedstock contained 79% maltene, soluble in n-hexane that included saturates, aromatics, hard and soft resin fractions, and 21% asphaltene, insoluble in n-hexane and soluble in toluene.

Cracking experiments were conducted in a 316-stainless steel batch reactor with an inner volume of about 12 ml. A schematic illustration of this reactor is presented in Fig. 2. In all experiments, the reactor was loaded with 150 mg VR and 4 ml distilled water, yielding a water/oil ratio (g/g): 80/3. For the cases of catalytic cracking 30 mg catalyst was added to the reactor that resulted catalyst/oil ratio (g/g): 1/5. The remaining air in the reactor was removed and purged by injecting nitrogen into the reactor, then it was capped tightly and put into an electric furnace adjusted to 450 °C. This temperature was recommended in several research works as an optimum value that yields a higher amount of light products, asphaltene conversion and prevents the coke formation [13, 15, 17]. Also, Fumoto et al. [33] reported that the generation of hydrogen and oxygen via the redox reaction of water and the catalyst was accelerated at 450 °C. It should be noted that the corresponding pressure inside the reactor calculated from the steam tables was about $P=45$ Mpa. After 60 min, reaction time, the reactor was removed from the furnace and was quenched by cold water bath so as to terminate any reactions. After cooling, the reactor contents were firstly recovered by washing the reactor with chloroform. A high speed centrifugation of 20 min at 12000 rpm was utilized to extract catalyst and coke deposited on the catalyst surface. The chloroform in the supernatant was allowed to evaporate completely and the resultant residue was afterwards collected in a beaker with about 20 ml of n-hexane. The solid phase was separated using a filtration and the n-hexane soluble fraction was defined as maltene. The solids left on the

filter were dissolved in about 20 ml of toluene and underwent a high speed centrifugation, 12000 rpm, for 20 min. Then, the supernatant was heated in a beaker at 70 °C overnight in order to vaporize the toluene. The solids that remain in the beaker were collected, weighted and considered as asphaltene. While, the solids remaining in the bottom of centrifuge tube were transferred to the Petri dish, dried at 70 °C overnight and weighed. This toluene insoluble fraction was defined as coke. The method mentioned above for the recovery of products illustrated in Fig. 1. It should be noted that the total amount of coke includes toluene insoluble product and probable remained coke on the surface of the catalyst that could be measured using the weight loss during calcination of the recovered catalysts at 650 °C for 12 h [17]. The asphaltene and coke yield were estimated based on the weight of initial sample loaded into the reactor and the products according to the equation below:

$$\text{asphaltene (coke) yield (wt\%)} = \left(\frac{\text{weight of asphaltene (coke) (g)}}{\text{weight of loaded VR (g)}} \right) \times 100 \quad (2)$$

As depicted in Fig. 1 maltene is extracted with n-hexane, but it is hard to separate all the maltene species from n-hexane to estimate the weight of the maltene. Hence, the maltene yield was calculated on the basis of asphaltene and coke yield:

$$\text{maltene yield (wt\%)} = 100 - \text{asphaltene yield} - \text{coke yield} \quad (3)$$

3. Results and Discussion

3.1. Catalyst

The XRD patterns of as-synthesized metal oxide nanoparticles are illustrated in Fig. 3. The patterns were compared to the references for the produced metal oxides according to the X-pert High Score PDF code, and thereby relevant compounds were detected. The well-resolved diffraction peaks shown in this figure indicate that the crystalline structure of the samples was

developed using SCW synthesis. The XRD broad peaks, especially for CeO₂ and Co₃O₄, are indicative of the particles with nanometric size. Nevertheless, transmission electron microscopy (TEM) images presented in Fig. 4 demonstrate better the size and morphology of the synthesized nanoparticles. The average diameter of the as-synthesized nanoparticles was calculated by CLEMEX software using measurement of the sizes of 500 particles in each TEM image. Accordingly, the average particle size of Co₃O₄, MnO₂, and CeO₂ nanoparticles are 38.9, 25.3, and 11.7 nm with the standard deviation of 11.5, 9.2, and 2.3, respectively.

The previous studies investigated the mechanism of metal oxide nanoparticles formation in supercritical water (SCW) [34, 35]: At the high temperatures, ionic product (K_w) of water increases significantly, leading to higher concentrations of [OH⁻] ions and therefore there would be a complete hydrolysis of the metal cations (M^{n+}) into the corresponding hydroxides (Eq. (4)). An increase in the temperature contributes to the decline in water dielectric constant and therefore the solvent power of water is decreased. Decreasing the solvent power of water increases the order of supersaturation and, in turn, contributes to the creation of a greater number of nucleation centers in their precipitation. In supercritical conditions the unstable transition metal hydroxides convert into metal oxides (Eq. (5)).

A modification for the metal oxide nanoparticles synthesis mechanism in SCW was made by introducing the formation and decomposition of an intermediate, namely metal hydroxynitrate complex in batchwise reactor [25]:

In the initial steps of the reaction, the reactor inner temperature is not high, so either a part of the metal nitrates or initially formed metal hydroxides (Eq. (4)) may transform into hydroxynitrate ($M_x(OH)_y(NO_3)_z$):

An increase in the temperature leads to the decomposition of hydroxynitrate complex to metal oxide nanoparticles:

Furthermore, Fig. 5 shows the FTIR spectra of three metal oxide nanoparticles revealing that all the samples exhibit a broadband and strong IR absorption in the region of 2800-3650 cm^{-1} with a band centered approximately at 3400 cm^{-1} corresponding to O–H stretching vibration; a band at ca. 2350 cm^{-1} may be due to the absorption of atmospheric CO_2 on the metallic cation [36], and a sharp band at ca. 1630 cm^{-1} attributed to the bending mode of the OH group of the adsorbed water molecules [37, 38]. In the spectrum of cerium oxide, the small peaks approximately at 1382, and 1515 cm^{-1} belong to the vibration of CeO_2 ; whereas the absorption band at about 540 cm^{-1} is related to Ce-O vibration [39, 40]. Two absorption bands at ca. 665 and 576 cm^{-1} in the spectrum of cobalt oxide are attributed to Co-O vibration mode in Co_3O_4 crystalline system [41, 42]. Also, in the spectrum of manganese oxide, the strong absorption peak situated approximately at 582 cm^{-1} is ascribed to the vibration of Mn-O [43, 44]. These results, in turn, confirm the development of crystalline phases for the nanoparticles synthesized via SCW method and are compatible with those obtained from the XRD patterns.

3.2. Performance of nanoparticles in vacuum residue cracking

In order to compare the ability of different nanocatalysts in upgrading of VR, the yields of maltene, coke, and asphaltene were calculated, based on the procedure described in section 2.3, and compared with non-catalytic cracking (Fig. 6). The operational condition was temperature: 450 °C, reaction time: 60 min, water/oil ratio (g/g): 80/3, and catalyst/oil ratio (g/g): 1/5 for the cases of catalytic cracking. The criterion for comparison was higher maltene yield and lower coke formation. As can be seen in Fig. 6, non-catalytic cracking had the highest amount of coke formation and the lowest maltene yield. On the other hand, all the three catalysts could attenuate the coke formation. This means that in the presence of the catalyst the asphaltene was mostly converted to the light products instead of coke. Fumoto et al. [32] reported that a catalyst can speed up the cleavage of the C–C bond in the cracking of petroleum residual oils, enhance the splitting of water, and thereby larger amount of hydrogen and oxygen species would be available to react with heavy fractions. CeO₂ exhibited a better performance compared with other nanocatalysts, whereas the catalytic effectiveness of MnO₂ was surprisingly frustrating. According to the results presented in Fig.6, the capability of different catalysts in cracking of VR can be ranged in the order of CeO₂, Co₃O₄, and MnO₂, while the non-catalytic cracking or SCW pyrolysis shows the worst performance. The effectiveness of different VR cracking processes, including catalytic and non-catalytic ones, can also be compared according to the change in the color of the recovered oil after reaction. Fig. 7 shows the recovered oils dissolved in a specified amount of n-hexane for different samples. The transparency of the recovered oil can be representative of the amount of light fractions in the final product. It is obvious that the brightness of the recovered oil for the samples changes in the same order obtained for VR cracking efficiency. Besides, the degree of stability of different catalysts after the reaction were evaluated by XRD analysis. For the sake of comparison the XRD patterns of fresh and spent

nanocatalysts are illustrated in Fig. 8. According to this figure, one can conclude that only CeO_2 could preserve its catalytic stability during the reaction, whereas both MnO_2 and Co_3O_4 suffered a phase transformation and were reduced to lower oxygen states.

The appropriate performance of CeO_2 in VR cracking can be attributed to its unique properties, namely high oxygen storage/release capacity and its stability in chemically harsh condition that exists in the SCW cracking of VR. It is worth noting that redox reaction between water, heavy oil, and the catalyst plays an important part in upgrading of heavy oil as well as stability of the catalyst. In a typical catalytic cracking of VR in SCW, the oxygen for oxidative cracking can be supplied from the catalyst leading to the reduction of it. The reduced catalyst can be regenerated by the active oxygen obtained from SCW, and thereby the redox cycle is completed. Hence, a metal oxide catalyst apt to easier conversion between its oxide states may present a better activity and stability. Since CeO_2 exhibited a great stability as well as an appropriate catalytic performance, one can notice that it possesses a better redox property than the other catalysts examined in this work, namely Co_3O_4 and MnO_2 .

3.3. Study on the stability and activity of CeO_2 nanocatalyst

In order to examine the activity as well as durability of CeO_2 against coke deposition and phase transformation during cracking, the catalyst was used in two sequential batch reactions. Accordingly, after the first sequence, the used catalysts from the first run were recovered from the reaction product dissolved in chloroform by using centrifugation (12000 rpm, 20 min). Then, the catalysts were treated with hot toluene so as to remove oil and coke attached to their surface, as much as possible. Finally, the catalysts were separated from any toluene insoluble components by means of filtration and dried in oven at 50 °C for 5 h. The operating conditions, including the temperature, reaction time, catalyst/oil, and the water/oil ratio, in the second sequence were

similar to the first one. Fig. 9 illustrates the XRD patterns of fresh CeO_2 along with the recovered catalysts after the first and second sequences. Noteworthy is the stability of ceria nanocatalyst after two successive reaction runs under such a harsh reaction conditions in which no peaks related to other phases of cerium oxide, i.e. Ce_2O_3 , and CeO were observed. As can be seen from Fig. 9, the XRD peaks pertaining to CeO_2 become narrower implying that the catalyst particles grow gradually through the reaction process. Moreover, the scanning electron microscopy (SEM) images of the recovered catalyst after the first and second sequences were taken in order to elucidate the particle growth (Fig. 10). The resultant images confirm the particle agglomeration due to the severe condition of SCW cracking.

As mentioned before, the total oxygen storage capacity (OSC) of ceria was estimated from H_2 -TPR. Fig. 11 gives the results of H_2 -TPR experiments on the fresh and spent catalysts, recovered after the first sequence, while the estimated values of total OSC along with measured BET surface area were presented in Table 2. As can be seen from this table, the ceria nanoparticles has a remarkable capacity of storage/release oxygen with excellent durability over the severe reaction period because no significant decline in the value of the total OSC was observed for the spent catalyst (less than 3%). Contrary, the BET surface area for spent catalyst decreased drastically owing to particle agglomeration. In both H_2 -TPR diagrams two distinct reduction peaks appeared at low and high temperature regions, namely 450-500 °C and 730-750°C, respectively. It was reported that the former is due to the reduction of the surface oxides, while the latter is attributed to the bulk oxides reduction [45-47]. Noteworthy is the slight difference in H_2 -TPR curves of the fresh and spent catalysts. The reduction peaks, especially one that corresponds to the surface reduction, of the spent catalyst only shift to lower temperatures and their height decrease contrary to the fresh one. It implies that the surface reduction of spent

catalyst occurred at a somewhat lower temperature, whereas its role was lessened. These results are in line with the finding of Fornasiero et al. [48], which found that the intensity of the H₂-TPR peak related to the surface reduction decreases with surface area of the CeO₂. They reported that the total OSC of the CeO₂ is strongly related to the presence of defective sites and consequently enhanced by increase of surface area. Furthermore, the shift of the H₂-TPR curve for spent catalyst can be attributed to the easier migration of lattice oxygen after a redox cycle[48].

For further information, the yield of maltene, coke, and asphaltene for the first and second sequences are presented in Fig. 12. It is obvious that the activity of the catalyst has declined during the second run so that the coke yield has increased and maltene yield has decreased compared with the first run. Bearing in mind that CeO₂ could preserve its catalytic properties such as oxidation state as well as total OSC, in one hand, and the sharp decline in BET surface area value, in the other, the reduction in catalyst activity is ascribed to the decrease of exposed area of the catalyst due to the particle agglomeration during the reaction sequences.

4. Conclusion

In this study, CeO₂, Co₃O₄, and MnO₂ nanoparticles were synthesized under supercritical water (SCW) condition using a batchwise reactor. Catalytic performance of the obtained nanoparticles was examined in vacuum residue (VR) cracking in SCW medium and was compared with non-catalytic operation. The results demonstrated the positive effect of nanocatalysts in the improvement of VR upgrading as well as in the suppression of coke formation. The catalytic performance of the metal oxide nanoparticles was found to decline in the order of CeO₂>Co₃O₄>MnO₂. In addition to the appropriate catalytic performance of CeO₂, only this nanocatalyst could be stable during SCW cracking experiment. The XRD patterns of the

recovered nonocatalysts after the reaction, confirmed the occurrence of a phase transformation to the lower oxidation states in the metal oxide nanocatalysts except CeO₂. Moreover, the activity and stability of CeO₂ nonocatalyst were scrutinized in the second sequence of the reaction. The values of the total oxygen storage capacity (OSC), estimated utilizing H₂-TPR test, showed a slight change for spent CeO₂ compared with the fresh one. The XRD results exhibited the stability of nanocatalyst in the second sequence, whereas the activity of the catalyst was partly decreased. The scanning electron microscopy (SEM) images of the spent catalysts after the first and second sequences represented the evidence of nanoparticles agglomeration. Since according the XRD and H₂-TPR results, CeO₂ nanoparticles could maintain its catalytic properties through successive reaction experiments, the decrease in catalytic activity attributed to the loss of the exposed surface area of the nanocatalyst resulted from the nanoparticles agglomeration.

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Reference

- [1] H. Alboudwarej, J. Felix, S. Taylor, R. Badry, C. Bremner, B. Brough, C. Skeates, A. Baker, D. Palmer, K. Pattison, Highlighting heavy oil, *Oilfield review*, 18 (2006) 34-53.
- [2] J.G. Speight, *The chemistry and technology of petroleum*, CRC press, 2014.
- [3] M. Morimoto, Y. Sugimoto, Y. Saotome, S. Sato, T. Takanohashi, Effect of supercritical water on upgrading reaction of oil sand bitumen, *The Journal of Supercritical Fluids*, 55 (2010) 223-231.
- [4] Z.M. Cheng, Y. Ding, L.Q. Zhao, P.Q. Yuan, W.K. Yuan, Effects of supercritical water in vacuum residue upgrading, *Energy & Fuels*, 23 (2009) 3178-3183.
- [5] K. Arai, T. Adschiri, M. Watanabe, Hydrogenation of hydrocarbons through partial oxidation in supercritical water, *Industrial & engineering chemistry research*, 39 (2000) 4697-4701.
- [6] T. Sato, P.H. Trung, T. Tomita, N. Itoh, Effect of water density and air pressure on partial oxidation of bitumen in supercritical water, *Fuel*, 95 (2012) 347-351.
- [7] P.Q. Yuan, Z.M. Cheng, X.Y. Zhang, W.K. Yuan, Catalytic denitrogenation of hydrocarbons through partial oxidation in supercritical water, *Fuel*, 85 (2006) 367-373.

- [8] M. Hosseinpour, S.J. Ahmadi, S. Fatemi, Successive co-operation of supercritical water and silica-supported iron oxide nanoparticles in upgrading of heavy petroleum residue: Suppression of coke deposition over catalyst, *The Journal of Supercritical Fluids*, 100 (2015) 70-78.
- [9] T. Adschiri, R. Shibata, T. Sato, M. Watanabe, K. Arai, Catalytic hydrodesulfurization of dibenzothiophene through partial oxidation and a water-gas shift reaction in supercritical water, *Industrial & engineering chemistry research*, 37 (1998) 2634-2638.
- [10] R.Z. Lee, F.T. Ng, Effect of water on HDS of DBT over a dispersed Mo catalyst using in situ generated hydrogen, *Catalysis today*, 116 (2006) 505-511.
- [11] T. Sato, T. Adschiri, K. Arai, G.L. Rempel, F.T. Ng, Upgrading of asphalt with and without partial oxidation in supercritical water, *Fuel*, 82 (2003) 1231-1239.
- [12] M. Hosseinpour, S. Fatemi, S.J. Ahmadi, Catalytic cracking of petroleum vacuum residue in supercritical water media: Impact of α -Fe₂O₃ in the form of free nanoparticles and silica-supported granules, *Fuel*, 159 (2015) 538-549.
- [13] T. Sato, S. Mori, M. Watanabe, M. Sasaki, N. Itoh, Upgrading of bitumen with formic acid in supercritical water, *The Journal of Supercritical Fluids*, 55 (2010) 232-240.
- [14] T. Sato, T. Tomita, P.H. Trung, N. Itoh, S. Sato, T. Takanohashi, Upgrading of bitumen in the presence of hydrogen and carbon dioxide in supercritical water, *Energy & Fuels*, 27 (2013) 646-653.
- [15] L.Q. Zhao, Z.M. Cheng, Y. Ding, P.Q. Yuan, S.X. Lu, W.K. Yuan, Experimental study on vacuum residuum upgrading through pyrolysis in supercritical water, *Energy & fuels*, 20 (2006) 2067-2071.
- [16] O.N. Fedyaeva, A.A. Vostrikov, Hydrogenation of bitumen in situ in supercritical water flow with and without addition of zinc and aluminum, *The Journal of Supercritical Fluids*, 72 (2012) 100-110.
- [17] M. Dehghani, T. Aida, M. Watanabe, S. Takami, D. Hojo, N. Aoki, T. Arita, A. Kishita, T. Adschiri, Catalytic cracking reaction of heavy oil in the presence of cerium oxide nanoparticles in supercritical water, *Energy & Fuels*, 27 (2013) 4624-4631.
- [18] T. Adschiri, Y. Hakuta, K. Sue, K. Arai, Hydrothermal synthesis of metal oxide nanoparticles at supercritical conditions, *Journal of Nanoparticle Research*, 3 (2001) 227-235.
- [19] P.E. Savage, Organic chemical reactions in supercritical water, *Chemical reviews*, 99 (1999) 603-622.
- [20] T. Adschiri, Y. Hakuta, K. Arai, Hydrothermal synthesis of metal oxide fine particles at supercritical conditions, *Industrial & engineering chemistry research*, 39 (2000) 4901-4907.
- [21] R. Viswanathan, R.B. Gupta, Formation of zinc oxide nanoparticles in supercritical water, *The Journal of supercritical fluids*, 27 (2003) 187-193.
- [22] M. Outokesh, A. Saket, S.J. Ahmadi, M. Hosseinpour, A.R. Khanchi, Comparative Study on Adsorption of Iodine Vapor by Silica-Supported Cu Nanoparticles and Micronized Copper, *Industrial & Engineering Chemistry Research*, 51 (2012) 15315-15323.
- [23] J.R. Kim, K.Y. Lee, M.J. Suh, S.K. Ihm, Ceria-zirconia mixed oxide prepared by continuous hydrothermal synthesis in supercritical water as catalyst support, *Catalysis Today*, 185 (2012) 25-34.
- [24] Y. Liu, W. Yao, X. Cao, X. Weng, Y. Wang, H. Wang, Z. Wu, Supercritical water syntheses of Ce_xTiO₂ nano-catalysts with a strong metal-support interaction for selective catalytic reduction of NO with NH₃, *Applied Catalysis B: Environmental*, 160 (2014) 684-691.
- [25] M. Golmohammadi, J. Towfighi, M. Hosseinpour, S.J. Ahmadi, An investigation into the formation and conversion of metal complexes to metal oxide nanoparticles in supercritical water, *The Journal of Supercritical Fluids*, 107 (2016) 699-706.
- [26] N.N. Nassar, A. Hassan, P. Pereira-Almao, Comparative oxidation of adsorbed asphaltenes onto transition metal oxide nanoparticles, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384 (2011) 145-149.
- [27] A.R.M. Daud, Partial Oxidative Cracking of Polycyclic Aromatic Compounds under Supercritical Water Conditions for Heavy Hydrocarbons Upgrading, in, Imperial College London, 2011.

- [28] N. Skorodumova, S. Simak, B.I. Lundqvist, I. Abrikosov, B. Johansson, Quantum origin of the oxygen storage capability of ceria, *Physical Review Letters*, 89 (2002) 166601.
- [29] F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, R. Rosei, Electron localization determines defect formation on ceria substrates, *Science*, 309 (2005) 752-755.
- [30] A. Migani, G.N. Vayssilov, S.T. Bromley, F. Illas, K.M. Neyman, Greatly facilitated oxygen vacancy formation in ceria nanocrystallites, *Chemical Communications*, 46 (2010) 5936-5938.
- [31] C. Sun, D. Xue, Size-dependent oxygen storage ability of nano-sized ceria, *Physical Chemistry Chemical Physics*, 15 (2013) 14414-14419.
- [32] E. Fumoto, T. Tago, T. Masuda, Production of lighter fuels by cracking petroleum residual oils with steam over zirconia-supporting iron oxide catalysts, *Energy & fuels*, 20 (2006) 1-6.
- [33] E. Fumoto, S. Sato, T. Takanohashi, Production of Light Oil by Oxidative Cracking of Oil Sand Bitumen Using Iron Oxide Catalysts in a Steam Atmosphere, *Energy & Fuels*, 25 (2011) 524-527.
- [34] T. Adschiri, K. Kanazawa, K. Arai, Rapid and continuous hydrothermal crystallization of metal oxide particles in supercritical water, *Journal of the American Ceramic Society*, 75 (1992) 1019-1022.
- [35] H. Hayashi, Y. Hakuta, Hydrothermal synthesis of metal oxide nanoparticles in supercritical water, *Materials*, 3 (2010) 3794-3817.
- [36] A.C. Taş, P.J. Majewski, F. Aldinger, Chemical Preparation of Pure and Strontium-and/or Magnesium-Doped Lanthanum Gallate Powders, *Journal of the American Ceramic Society*, 83 (2000) 2954-2960.
- [37] B. Stuart, *Infrared spectroscopy*, Wiley Online Library, 2005.
- [38] P.B. Coleman, *Practical sampling techniques for infrared analysis*, CRC Press, 1993.
- [39] B. Yan, H. Zhu, Controlled synthesis of CeO₂ nanoparticles using novel amphiphilic cerium complex precursors, *Journal of Nanoparticle Research*, 10 (2008) 1279-1285.
- [40] S. Phoka, P. Laokul, E. Swatsitang, V. Promarak, S. Seraphin, S. Maensiri, Synthesis, structural and optical properties of CeO₂ nanoparticles synthesized by a simple polyvinyl pyrrolidone (PVP) solution route, *Materials Chemistry and Physics*, 115 (2009) 423-428.
- [41] M. Salavati-Niasari, N. Mir, F. Davar, Synthesis and characterization of Co₃O₄ nanorods by thermal decomposition of cobalt oxalate, *Journal of Physics and Chemistry of Solids*, 70 (2009) 847-852.
- [42] M. Herrero, P. Benito, F.M. Labajos, V. Rives, Nanosize cobalt oxide-containing catalysts obtained through microwave-assisted methods, *Catalysis Today*, 128 (2007) 129-137.
- [43] F. Pagnanelli, C. Sambenedetto, G. Furlani, F. Vegliò, L. Toro, Preparation and characterisation of chemical manganese dioxide: Effect of the operating conditions, *Journal of Power Sources*, 166 (2007) 567-577.
- [44] K.Q. Ding, Cyclic Voltammetrically-Prepared MnO₂ Coated on an ITO Glass Substrate, *Journal of the Chinese Chemical Society*, 56 (2009) 175-181.
- [45] H. Yao, Y.Y. Yao, Ceria in automotive exhaust catalysts: I. Oxygen storage, *Journal of Catalysis*, 86 (1984) 254-265.
- [46] M.F. Johnson, J. Mooi, Cerium dioxide crystallite sizes by temperature-programmed reduction, *Journal of catalysis*, 103 (1987) 502-505.
- [47] J.R. Kim, W.J. Myeong, S.K. Ihm, Characteristics of CeO₂-ZrO₂ mixed oxide prepared by continuous hydrothermal synthesis in supercritical water as support of Rh catalyst for catalytic reduction of NO by CO, *Journal of Catalysis*, 263 (2009) 123-133.
- [48] P. Fornasiero, R. Dimonte, G.R. Rao, J. Kaspar, S. Meriani, A.-. Trovarelli, M. Graziani, Rh-loaded CeO₂-ZrO₂ solid-solutions as highly efficient oxygen exchangers: dependence of the reduction behavior and the oxygen storage capacity on the structural-properties, *Journal of Catalysis*, 151 (1995) 168-177.

Figures Caption

Fig. 1. The procedure for recovery of products and catalyst according to ASTM D6560-00.

Fig. 2. A schematic sketch of batch stainless steel reactor.

Fig 3. X-ray diffraction patterns of nanoparticles produced in supercritical water.

Fig. 4. Transmission electron microscopy (TEM) images of synthesized nanoparticles: (a) CeO_2 , (b) Co_3O_4 , and (c) MnO_2 .

Fig 5. Fourier-transform infrared spectroscopy (FTIR) spectra of metal oxide nanoparticles synthesized in supercritical water.

Fig. 6. Comparison of the maltene, coke, and asphaltene yield obtained from SCW catalytic cracking/pyrolysis of VR. ($T = 450\text{ }^\circ\text{C}$, $t = 60\text{ min}$, water to oil ratio (g/g): 80/3, and catalyst to oil ratio (g/g): 1/5).

Fig. 7. Recovered oil dissolved in n-hexane obtained from: (a) catalytic cracking with CeO_2 , (b) catalytic cracking with Co_3O_4 , (c) catalytic cracking with MnO_2 , (d) noncatalytic cracking, and (e) unreacted VR.

Fig. 8. X-ray diffraction patterns of fresh and recovered nanocatalysts after the reaction. ($T = 450\text{ }^\circ\text{C}$, $t = 60\text{ min}$, water to oil ratio (g/g): 80/3, and catalyst to oil ratio (g/g): 1/5).

Fig. 9. Comparison of X-ray diffraction patterns of fresh and recovered CeO_2 nanocatalysts after successive reaction runs. ($T = 450\text{ }^\circ\text{C}$, $t = 60\text{ min}$, water to oil ratio (g/g): 80/3, and catalyst to oil ratio (g/g): 1/5).

Fig. 10. Scanning electron microscopy (SEM) images of the CeO_2 : (a) after first sequence and (b) after second sequence. ($T = 450\text{ }^\circ\text{C}$, $t = 60\text{ min}$, water to oil ratio (g/g): 80/3, and catalyst to oil ratio (g/g): 1/5).

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

M_w (mol/g)	ρ_4^{20} (g/cm ³)	ν^{80} (mm ² /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

Table 2. BET surface area and total OSC of CeO₂ before and after catalytic cracking of VR (T = 450 °C, t = 60 min, water to oil ratio (g/g): 80/3, and catalyst to oil ratio (g/g): 1/5).

BET surface area (m ² /g)		Total OSC (μ mol O ₂ /g)	
Fresh	After the first sequence	Fresh	After the first sequence
107.6	25.3	786	765

CeO₂

Co₃O₄

MnO₂

Noncatalytic

Unreacted VR

Recovered oil after cracking in SCW