The Effects of Ph and Chelating Agent on Characterization of Ni Mo/-Alumina Heavy Oil Hydrodesulphurization Nanocatalyst

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Abstract:
This study reports the synthesis of mixed oxides of Mo, and Ni nanostructures on γ- Alumina as support, by utilizing ammonium hepta molybdate(AHM), nickel nitrate, as precursors, and organic additives such as citric acid, ethylene diamine tetra acetic acid (EDTA), and urea were used as chelating agent and different pH, in order to investigate the effects of additive structure and pH variation on chemical and physical properties, morphology, size of nanocatalyst and interaction of active metals with support. Also, this study evaluated the activity of catalysts and compare with commercial catalyst. The metal oxide nanoparticles were prepared and impregnated using wetness impregnation method on γ- Alumina in-situ. The supported nanocatalyst was calcined to remove the volatile material and gases. The nanocatalyst prepared using organic additive,EDTA as surfactant showed enhanced catalytic activity for the oil residue hydrodesulphurization which contained 21000 ppm sulfur. The sulfur content of the feed was reduced to 3000 ppm at 380°C and LHSV 1.5h-1 showing a good catalytic activity.

Keywords: Molybdenum oxide, Nanostructures, Hydrodesulphurization, chelating agent, heavy oil.

1. Introduction:
Oil residue is one of the cuts of the oil refinery process, and it consists of more than 4% sulfur. The sulfur in oil residue is a poison for catalysts of other processes in a refinery. Therefore, there is need for desulphurization. Highly active catalysts have been prepared through several strategies, such as in situ activation that was performed in the presence of a hydrocarbon solvent[1], modification of support [2-7], use of different additives such as phosphorus, fluoride and lanthanum have been added to the alumina support for the development of the required catalytic properties [2]. The use of new supports with specific physiochemical properties, such as nanoporous carbon [7]. One of the strategies followed to get more efficient hydrotreating catalysts consists in developing novel carriers that could contribute in obtaining enhanced properties of supported sulfide CoMo or NiMo active phases [3]. HDS of DBT and gas oil has been carried out on ASA-supported TMS(transition metal sulphides) under conditions which approach industrial practice[4].

Another strategy is the use of unsupported catalysts for the hydrodesulphurization of oil feed, such as unsupported MoO3 nanostructure [8], unsupported Ni-Zn-Mo catalyst [9], unsupported materials with higher activity and/or selectivity than the traditional gamma alumina supported Ni/Co-Mo/W catalysts [10-11], Mo nanoparticles using γ-radiation[12]. The use of an advanced oxidation method for producing a very strong oxidant agent that reacts with the sulfur component is a desulphurization method [13]. In recent years, there has been a considerable interest in the synthesis and characterization of nanoparticles. Nanoparticles often exhibit novel properties which are different from the bulk materials` properties. Many of these properties showed a strong dependence on size, shape, and surface preparation. The characterization of these properties can ultimately lead to the identification of many potential uses, particularly in the field of catalysis. Another efficient method of obtaining high activity is by the synthesis of ultra-small NiMo bimetallic Nano clusters on γ- Alumina [14], and it can be concluded that the higher activities of nano clusters on γ- Alumina may be due to the better dispersion or smaller particle size compared to the non-nano catalyst. The smaller crystal size results to a greater number of CUS(coordinately unsaturated) sites or anion vacancies. These anion vacancies or cus sites are responsible for HDS catalytic activities; hence, nanoparticles on Al2O3 supported catalysts showed higher activities [7].

In this study, to improve the activity of the desulphurization catalyst, by the use of organic additives as chelating agent, MoO3 and NiO nanostructure on γ- Alumina as support were synthesized and the effects of impregnation conditions
such as media pH and kind of organic additives on active metals morphology, size, amount, their interaction on support and catalyst performance were precisely investigated.

2. Experimental

2.1. Catalyst preparation

An $\gamma$-Alumina (surface area 250 m$^2$g$^{-1}$, pore volume 0.78 cm$^3$g$^{-1}$, pore diameter 12.6 nm) was typically used as support. The nanocatalysts were prepared by contacting the supports with 10 ml of metal precursors solution and organic additive at a pH close to 4. For the preparation of Mo and Ni catalysts, the employed precursors were: Ammonium heptamolybdate (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O (Merk, reagent grade), nickel nitrate Ni(NO$_3$)$_2$.6H$_2$O, citric acid (C$_6$H$_8$O$_7$), ethylene diamine tetra acetic acid (EDTA), urea (NH$_4$)$_2$CO. After contacting $\gamma$-Alumina support with the impregnating solution for 6h, at a temperature of 60°C, the excess water was evaporated, then catalysts were dried at 120°C for 2h, and calcined in a 2-step procedure: first at a rate of 2°C min$^{-1}$ to 300°C and maintaining this temperature for 2h and then raising temperature to 520°C followed by isothermal calcination at that temperature for 5h.

2.2. Characterization techniques

Metal contents were determined by atomic absorption spectrometry using a GBC avanta Absorption instrument. The samples were solubilized in a solution of H$_2$SO$_4$. X-ray diffraction (XRD) analysis of the samples was carried out using a X’pertpro from panalytical company diffractometer with a Cukα monochromasied radiation source (λ = 1.54056 Å), operated at 40 kv and 40 MA. The morphologies of the prepared samples were studied using a scanning electron microscope (SEM), operated at 20 kv. By using the energy dispersion X-ray spectrum (EDX) detector as recorder, elemental mapping was conducted under scanning transmission electron microscopy (STEM) mode. Specific surface area measurements were performed on a belsorb miniII instrument by nitrogen adsorption at 77k using the BET isotherm while the pore size distribution was calculated by N2 adsorption using the Barret–Joyner–Halleda (BJH) method. Temperature-programmed reduction (TPR) profiles were obtained on a Micromeritic – 2900 apparatus interfaced with a computer. A sample of 0.1 g was housed in a quartz tubular reactor and the TPR profiles were obtained by passing a 10% H$_2$/Ar flow (22 ml min$^{-1}$) through the sample at temperatures from 30°C to 1000°C. The temperature was increased at a rate of 10°C min$^{-1}$ and the amount of H$_2$ consumed was determined with a thermal conductivity detector (TCD).

2.3. Activity tests:

The HDS reaction of a 50/50 diluted oil residue with gas oil was performed in a low- pressure laboratory scale set-up equipped with a stainless-steel fixed bed catalytic reactor (20 mm i.d. and 230 mm length). The activity test procedure consisted of catalyst drying, sulpidizing, process stability and sampling. The reaction conditions for the HDS of oil residue were: T= 400°C, P= 60 barg, LHSV= 1.5h$^{-1}$, H$_2$/H.C. = 1000Nm$^3$/m$^3$. The sulfide form of the NiMo/$\gamma$-Alumina catalyst was regarded as the active form of the hydrosulphurization catalyst; therefore, before evaluating the HDS activity of the catalyst, the catalyst underwent sulpidizing. Using 2wt% of dimethyl disulfide (DMDS) dissolved in gas oil. The sulpidizing procedure was as follows: (i) the catalyst temperature was first increased at 10 bar pressure to 150°C in 120 min under a H2 flow of 19 l/h. (ii) when the temperature reached 150°C, the catalyst was kept at this temperature for 4h, during this time, the reactor pressure was increased to 60 bar. The sulpidizing feed (0.55ml/min) was started when the reactor pressure had reached 60 bar. (iii) the temperature was then increased from 150 to 220°C in 120 min and the catalyst was kept at this temperature for 60 min . (iv) the catalyst temperature was increased from 220 to 360°C in 240 min and kept at this temperature for 60 min. After sulpiding the HDS activity, the catalyst was investigated at a pressure of 60 bar in a temperature range of 380-400°C. The liquid feed was diluted oil residue having gasoil with 21000 ppm sulfur, and 5g of the catalyst was used. The flow rate of hydrogen was 13.5 l/h and the flow rate of the liquid was 13.5ml/h. The catalyst was stabilized for at least 12 h, before acquiring the conversion data.
Results and discussion:

For the synthesis of a catalyst possessing the ability of the HDS reaction of an oil feed with further activity, MoO₃, NiO nanoparticles were impregnated on γ-Alumina and the effects of organic additives and the pH of the media were investigated on characterization of catalyst and performance test was conducted in a low pressure laboratory scale – up and the activity was compared with commercial catalyst on sulfur decreasing. The active metal of the catalysts was Mo. For synthesis, the MoO₃ nanoparticles was used from ammonium hepta molybdate (AHM), that is a big complex molecule which is usually used as a precursor in the preparation of molybdenum compounds. Also, nitrate nickel was used as a precursor in NiO compound preparation. AHM in solution with temperature, without organic additives via the following reaction will be completed which will form a long molecular chain. However, when organic additives are used in reaction, distances between particles will be created. Organic additives as chelating agent will direct MoO₃ nuclei formation and growth.

\[(NH_4)_6Mo_7O_{24}.4H_2O \rightarrow MoO_3 + 6 NH_3 + H_2O\]

Active sites and reaction mechanism of catalyst

HDS catalysts are based on molybdenum sulfide, along with a small amount of other metals. There are two types of active sites for MoS₂. The hydrogenation carried out on rim sites and HDS on rim and edge sites. The crystalline structure of catalyst consists bridges of sulfur with Mo in the center and unsaturated active sites. In the bonding of sulfur compounds with active sites, C=S bond is broken and hydrogenolysis is occurred and C=C bond is hydrogenated. H₂ in the reaction with sulfur of catalyst and elimination of H₂S, activates reaction sites again. So H₂ has responsibility of hydrogenation, hydrogenolysis and generation of anionic active site, the figure 1 shows mechanism of reaction [19].

![Reaction mechanism of catalyst](image)

Fig 1: reaction mechanism of catalyst

The composition and stability of catalyst

Before activation, Catalyst composition was MoO₃, NiO on γ-Alumina. Most of hydrodesulphurization catalysts have similar composition, but according to the preparation process performance and crush strength of catalysts are different [25]. The table 1 is shown typically catalyst composition.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>MoO₃</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MnO</th>
<th>L.O.I</th>
<th>2018.0384.v1</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
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<td></td>
<td>0.26</td>
<td>0.006</td>
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<tr>
<td>MoO₃</td>
<td></td>
<td>10.65</td>
<td>69.58</td>
<td>2.01</td>
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<td></td>
<td>0.006</td>
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<tr>
<td>Al₂O₃</td>
<td>69.58</td>
<td></td>
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<td></td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
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<td></td>
<td>0.087</td>
<td>0.07</td>
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</tr>
<tr>
<td>CaO</td>
<td>0.26</td>
<td></td>
<td>0.09</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td></td>
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<td>0.02</td>
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<td>L.O.I</td>
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<td></td>
<td>P₂O₅</td>
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</tr>
</tbody>
</table>

Table 1: Composition of commercial catalyst with XRF
In the HDS catalysts, precursor concentration determines the type of molecular structure of Mo. For example, if the concentration of molybdenum, in the solution, is less than 3% by weight, after the calcination process, the four coordinate monomeric structure of Mo is obtained ($\text{MoO}_4^{2-}$) [20-22]. If the concentration of Mo in solution is more than 7% wt, the polymer structure with six coordinate of Mo will be formed (MoO$_3$). On the other hand, the molecular structures are dependent on solution PH of Mo. In low concentration and PH>4 four ($\text{MoO}_4^{2-}$) or six ($\text{MoO}_3$) coordinate monomeric species are produced [23]. In the high concentration of Mo, octa and hepta structures are produced [23-24]. In the presence of free ions Al$^{3+}$, a special structure is represented by the formula $[\text{Al (OH)}_6\text{Mo}_6\text{O}_{18}]^{3-}$ or $[\text{AlMo}_6]$. According to the following reaction, Al ions are produced by dissolving Al$_2$O$_3$ and in the reaction with MoO$_4^{2-}$-mentioned ion is formed.

$$\text{Al}_2\text{O}_3 + 15 \text{H}_2\text{O} \rightarrow 2 \text{Al (H}_2\text{O)}_6^{3+} + 6 \text{OH}^-$$

$$6 \text{MoO}_4^{2-} + \text{Al (H}_2\text{O)}_6^{3+} + 6 \text{H}^+ \rightarrow [(\text{Al(OH)})_6\text{Mo}_6\text{O}_{18}]^{3-} + 6 \text{H}_2\text{O}$$

The polymer structure can convert to monomer structure in the surface of catalyst.

$$\text{Mo}_7\text{O}_{24}^{6-} + 8 \text{OH}^- \rightarrow 7 \text{MoO}_4^{2-} + 4 \text{H}_2\text{O}$$

$$[(\text{Al(OH)})_6\text{Mo}_6\text{O}_{18}]^{3-} + 6 \text{OH}^- \rightarrow \text{Al}^{3+} + 6 \text{MoO}_4^{2-} + 6 \text{H}_2\text{O}$$

Fig 2: Mo different species in the different pH

The calculation shows that, in concentration of more than 6.3 wt% of molybdenum, AlMo$_6$ and in less than 6.3 wt%, hepta molybdat are dominant species in the catalysts [26].

Stability of catalyst depends on interaction of support – active metal. If the precursor concentration is low, these interactions would cause the surface absorption of metal anion on support. And in the more concentration of precursor, aggressive species on support, after drying, became crystalline. There are two types of phases for Ni-Mo-S [27]. The type I phase from Ni-Mo-S, with strong interaction between support and active metal and less sulfidation (causes bonding of Mo-Al-O). In the phase II of Ni-Mo-S, all of the particles are sulfurized and is kept on support by vandervalce forces. Phase II is more activity than phase I but phase II is more stable. In this catalyst, using of chelate agent is caused forming of Ni-Mo-S active phase II on support and active species is distributed on alumina surface. Chelate additive help to distribution of active species on support and to decreasing of interaction between Mo,Ni with
support until the formation of the sulfide active phase II [28-29]. In addition, in presence of the chelate ligand, in higher temperature, sulfudation of Ni is began, after sulfudation of Mo or simultaneously. So it is possible that Ni is taken in edges of MoS and increased active phase Ni-Mo-S and, the possibility of CO separation decreases individually [30].

The activity of catalysts in during reactions is changed and reduced with time in the petroleum refineries. Rate of deactivation is important and difference for different catalysts. For evaluation of catalyst performance or stability in the pilot plant souled be performed similarly to the refinery process, due to the impossibility, Accelerated deactivation technique is used [31].

In the hydrotreating catalysts, deactivation occurs in order to the poisoning and closure of the catalyst pores with toxic metals such as vanadium and nickel in the heavy oil and sintering of active sites and coke formation on the catalyst surfaces. The results of accelerated deactivation of synthesized catalysts in presence chelate agent and commercial catalyst is shown that conversion of catalyst in desulfurization have decreased after deactivation of catalyst. Sulfur and Ni- V content in heavy oil feed is 1.11 %wt. and 53 ppm respectively.

![Graph showing sulfur conversion and activity comparison](image_url)

**Fig 3:** The results of accelerated deactivation of synthesized catalysts in presence chelate agent and commercial catalyst

The effect of organic additives on the chemical and physical properties of the catalyst

Previous researches evaluated the effect of various organic additives on MoO₃ nanoparticle formation and growth [2]. In this research, three organic additives, EDTA, citric acid and urea were selected based on size, ligand dents and acidity, followed by the examination and investigation of their effects on MoO₃, NiO nanoparticle amount of active metal that was impregnated on support from impregnation solution as well as the chemical and physical properties of the catalyst. All the additives were examined in similar reaction conditions in order to find the effects on catalysts.

The reaction conditions in the presence of all the additives were similar. The pH of the reaction medium was acidity, the synthesis temperature was kept at 60°C, and calcination temperature was kept at 520°C. The results of these experiments are presented in Table 2.
Table 2: chemical and physical properties of catalyst

<table>
<thead>
<tr>
<th>Organic additive</th>
<th>urea</th>
<th>Citric acid</th>
<th>EDTA</th>
<th>support</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo ( ppm)</td>
<td>40.8</td>
<td>87.5</td>
<td>138.2</td>
<td></td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>11.8</td>
<td>15.1</td>
<td>19.1</td>
<td></td>
</tr>
<tr>
<td>Surface area M²/g</td>
<td>236</td>
<td>217</td>
<td>260</td>
<td>250</td>
</tr>
<tr>
<td>pore volume (P.V)cm³/g</td>
<td>0.63</td>
<td>0.55</td>
<td>0.64</td>
<td>0.78</td>
</tr>
<tr>
<td>pore diameter(P.D.)nm</td>
<td>10.7</td>
<td>10.1</td>
<td>9.9</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Condition: PH = 3.5, Reaction temperature = 60°C, Calcination temperature = 520°C

The results showed that the performance of EDTA is better than citric acid and urea, citric acid is better than urea, in the nuclei formation of impregnation solution and interaction of active metal with support and increasing of surface area, it means that the properties of the catalyst improved. EDTA is a useful amino carboxylic acid because it plays the role of a six-dent ligand and its chelating function can separate metal ions. Metal ions can bind with EDTA and remain in the solution. The main functional groups in EDTA are two nitrogen atoms and four oxygen atoms. Therefore, further ions were removed from the complex, and impregnated on the support and the surface area was increased, while citric acid which has four-dents and four oxygen atoms bonded with metal, but in urea, only two nitrogen atoms as functional groups can extract Mo ions from the AHM complex structure.

The effect of reaction media pH on catalyst properties

The pH of the reaction medium is an important parameter in catalyst synthesis and impregnation of solution. When using an additive in solution, the effect of pH on catalyst properties depend on the nature of the additive. In other words, the presence of H⁺ or OH⁻ groups in the solution could affect the activity of the functional groups of additives. To investigate this parameter, pH variation was performed in the presence of urea and citric acid as chelating agents. The amount of Mo, Ni on support was determined by AAS. The results of these experiments are shown in Table 3.

Table 3: effect PH on interaction of Mo, Ni as metal active

<table>
<thead>
<tr>
<th>PH</th>
<th>5</th>
<th>7</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(ppm)</td>
<td>114</td>
<td>134.9</td>
<td>128.5</td>
</tr>
<tr>
<td>Ni(ppm)</td>
<td>16.4</td>
<td>20</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Condition: chelate agent: urea

Reaction temp. : 60°C
Calcination temp. : 520°C

The results in Table 3 showed that interaction urea with active metals in neutral pH is better than basic or acidic pH. Previous studies have shown that the morphology of MoO₃ in the presence of urea at pH = 7 is nanorod and in basic pH it is microrod but in acidic pH it is nano spherical. Therefore, it was concluded that nanorod morphology has
stronger interaction with support. Also, the surface area, pore volume, and pore diameter of two nanocatalysts in acidic pH were compared in the table 4.

Table 4: comparing of Physical properties of nano catalyst in two PH

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Surface area (M2/g)</th>
<th>pore volume (P.V. cm3/g)</th>
<th>pore diameter (P.D. nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH = 3.5</td>
<td>236</td>
<td>0.63</td>
<td>10.7</td>
</tr>
<tr>
<td>PH = 5</td>
<td>254</td>
<td>0.72</td>
<td>11.29</td>
</tr>
</tbody>
</table>

Condition: chelate agent: urea
Reaction temp.: 60°C
Calcination temp.: 520°C

The results showed that the increase in pH from 3.5 to 5 improved the physical properties of the nano catalysts. For more investigation, the XRD patterns of nano catalysts obtained by urea in different pH were compared.

Table 5: Peak height of MoO3 in different PH

<table>
<thead>
<tr>
<th>PH</th>
<th>5</th>
<th>7</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak height of MoO3</td>
<td>154</td>
<td>117</td>
<td>153</td>
</tr>
</tbody>
</table>

Fig 4 and Table 5 show the XRD patterns for the synthesized nano catalyst using different pHs. As was expected, nano catalysts were synthesized in pH = 7, and a comparison of nano catalysts in basic and acidic media showed less sharp peak because the morphology of MoO3 in this catalyst is nanorod. By increasing the pH of the basic solution, MoO3 morphology will lead to the micron. These results were confirmed by SEM image and the TPR patterns of the nano catalysts synthesized in media with acidic and basic pH and compared.
Fig. 5: SEM images of samples prepared with urea in the: a) pH= 3.5, b) pH= 7, c) pH= 9
Fig. 6: SEM images of samples prepared with EDTA in the: a: pH = 3.5, b: pH = 5, c: PH = 7, d: PH = 9
The particle morphology and elemental distribution in the nanocatalysts were investigated using Scanning Electron Microscopy. Fig. 5 shows SEM micrographs of the typical synthesized nanocatalysts with urea as chelating agent in the different PHs. Spherical nano particles are formed in an acidic solution (PH=3.5) when urea is used as chelating agent. When adjusting the PH to 7 and increasing the PH of solution to 9, most of the spherical particles are converted into larger particles, will led to the formation of micron. When using EDTA as chelating agent, by increasing the PH of reaction media from 3.5 to 9, the particles became thicker and longer (Fig. 6). The SEM images revealed that the dispersion of metals in acidic pH is better than in basic pH.

TPR RESULTS

The reductive abilities of catalysts were studied by H$_2$-TPR and the results are shown in Figs. 7, 8. Hydrogen consumption is an index which shows catalyst performance, metal dispersion and active sites. The TPR results of the synthesized catalysts in the different PH showed that, in the use of citric acid and urea as a chelating agent, hydrogen consumption in acidic pH is more compared to basic pH. In the acidic PH, the reductive abilities of catalysts, in the use of urea and citric acid are similar, but in the basic PH, citric acid is better compared to urea as chelating agent. So it can be concluded, that in the acidic PH with both of chelating agents, H$_2$- consumption is more compared to basic PH. The comparative TPR analysis for nanocatalysts using urea in the acidic and basic PH is shown in Fig. 5. The reduction profile of nanocatalyst prepared in the acidic PH shows hydrogen consumption in a broad temperature interval (between 300 and 1000°C) with two main reduction peaks at 497°C and 827°C. The lower temperature peak (497°C) can be attributed to the first step of reduction (from Mo$^{6+}$ to Mo$^{4+}$). The peak at 827°C can be ascribed to the reduction of Mo$^{4+}$ to Mo$^{0}$ [15-18]. Similarly, two main reduction peaks were observed for nanocatalyst prepared in the basic PH, with a shift in reduction position towards higher temperature. The shift in first and second reduction peaks was 10°C and 30°C, respectively. The TPR results and area of peaks show that nanocatalyst prepared in acidic PH is more reducible and active sites in comparison to basic nanocatalyst. The both of catalysts showed a small reduction peak at 580-600°C due to the reduction of Ni$^{2+}$ to Ni$^{0}$.

![Fig. 7: TPR profiles of samples prepared urea and citric acid in the acidic and basic PH](image-url)
Fig 8: TPR profiles of samples prepared by urea in the acidic (a) and basic (b) PH
Catalytic activity for hydrodesulphurization

To compare the activity of catalysts, a real HDS was conducted with two catalysts that were synthesized in acidic pH with citric acid and urea and were compared with a commercial catalyst. Diluted oil residue with gas oil was used as a feed stock for hydrotreating and the catalytic activity was determined in terms of percentage removal of sulfur compounds present in the feed. The processes were termed as hydrodesulfurization (HDS). The hydrotreating reaction was carried out in a continuous fixed bed reactor at laboratory conditions of 60 bar pressure, 1.5 L/h LHSV and H2/H.C. ratio of 1000 at 400°C temperature. The HDS conversions for two catalysts and comparison with commercial catalyst are presented in Fig. 9 and Table 6.

Table 6: The HDS conversions for two catalysts and comparison with commercial catalyst

<table>
<thead>
<tr>
<th>Cat. Type</th>
<th>Comm. Cat.</th>
<th>Cat. With EDTA</th>
<th>Cat. With citric acid</th>
<th>Cat. With urea</th>
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<tbody>
<tr>
<td>Sulfur conversion (%)</td>
<td>94</td>
<td>90</td>
<td>88</td>
<td>84</td>
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</table>

Fig. 9. HDS activity of supported nano catalyst with oil residue 400°C (catalyst= 5 g, p= 60 bar, LHSV= 1.5, H2/H.C. = 1000)

Conclusion

In this work, a variety of nanocatalysts with a variety of chelating agents were synthesized and were used as HDS catalyst. The chelating agent was varied to obtain a series of nanocatalysts with different physical and chemical characteristics. The synthesized catalyst with EDTA of 6 dents presented maximum surface area, pore volume of 260 m²/g, and 0.64 cc/g, respectively. The utilization of urea resulted to the formation of nanoparticles, whereas EDTA facilitated the formation of nano rods. A variety of pH media showed neutral pH toward basic and acidic pH, the increased interaction of Mo, Ni nanoparticle on the support and XRD patterns of the nanocatalyst in the neutral pH confirmed the nanorod morphology. SEM images and H2-TPR studies showed that in the acidic pH, metal dispersion
on support, active sites and the reductive abilities of catalysts were better compared to a medium with basic pH. Ultimately, it can be concluded that nanocatalysts were synthesized with different chelating agents, this means that the supported NiMo hydro treating catalysts, showed comparable HDS activities. The catalyst with EDTA had the required physicochemical properties to be a suitable hydro treating catalyst.

References