Slurry Phase Hydrocracking of Residue by Phosphomolybdic and Phosphotungstic Acids

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Abstract

Slurry phase hydrocracking of vacuum residue was studied on heteropoly acids and on super acid. In this regards, heteropoly acid of phosphomolybdic, phosphotungstic and superacid of molybdenum-antimony fluoride were used. Deep hydrocracking of residue was noticed even at moderate operating conditions for all acidic catalysts. Due to higher hydrogenating functionality of tungsten, the HDM activity of the phosphotungstic acid is higher than that of molybdenum containing acids. Even the residue hydrocracking activity of former catalyst is also high. It is also noticed from sulphur distribution of liquid product that thiophenic sulphur compounds are formed due to C-S bond cleavage at branching of condensed aromatic rings. Moreover, phosphotungstic acid gives high percentage of aromatic products whereas the considerable amount of saturate hydrocarbons is produced by phosphomolybdic acid. The coke produced by phosphotungstic acid catalyst is hard in nature indicating that extensive polymerization reaction occurs at reaction conditions. Higher H/C ratio indicates the deep hydrogenation of liquid products in presence of superacid. Instead of use superacid, tungsten based heteropoly acid can be effectively used for hydrocracking of residue.

Keywords: Superacid; Heteropoly acid; Residue conversion; Slurry phase; FT-IR; TGA

Introduction

The future demand of transportation fuel can be fulfilled by upgrading unconventional reserves of heavy oil [1]. The amount of extra-heavy oil and bitumen is predicted to be around 5.4 trillion barrels. This heavy oil and bitumen contain high concentrations of heteroatoms like sulphur, nitrogen, carbon residue and metal contents like Ni, V. Due to the presence of high percentage of carbon residue, hydrocracking of heavy oils and their residue is challenging for refiners. In this respect, the acid functionality of a catalyst has an important role for residue hydrocracking. In a conventional supported catalyst, Lewis acid sites are used. In a typical catalyst system, metals like Mo, W, Ni, and Co are impregnated on acidic support like alumina; alumina based mixed oxide, modified zeolite and other support having acid sites [2-5]. However these supported catalysts are deactivated rapidly due to pore plugging by metal, and coke. Moreover, the coke deposit increases with increasing the acidity of the supported catalyst. The rapid deactivation of the supported catalyst can be avoided if unsupported catalyst is used in slurry phase hydrocracking. Heteropoly acid is an alternative of acidic supported catalyst for residue hydrocracking. Sometimes, this super solid acid is modified by active metals like, Mo and W to increase the hydrogenation functionality. The hydrogenation functionality reduces coke formation during hydrocracking reaction.

Hydrocracking activity of phosphotungstic acid was compared with a conventional NiMo supported catalyst [6]. Cs exchange on the acidic catalyst was made to obtain appropriate physicochemical property of the catalyst. Compared with a conventional catalyst, higher hydrocracking activity of Cs-phosphotungstic catalyst was reported. Moreover, the removal of metals and sulphur of acidic catalyst was also comparable with the supported catalyst. For coal liquefaction, Olah et al. [7-9] extensively used superacid. Authors have shown that HBF$_3$ based superacid could be good catalyst for conversion of tar sand. The depolymerisation of coal took place during hydroliquefaction reaction. The product had more than 90% pyridine solubility indicating the higher conversion of coal to lighter hydrocarbons. It was also reported that in the presence of acidic environment, comparatively less temperature was required. A highly reactive superacid like ethyl fluoride: antimony pentfluoride complex are used for alklylation reaction of coal [9]. It was also reported by others [10,11] that superacids can be prepared by metal halides with anhydrous HF and their hydrocracking activity was tested. Hydrocracking activity of tar sand bitumen and asphaltene by HR.BF$_3$ superacid was also studied by Strausz et al. [12]. It was reported that this superacid was very effective for both aliphatic and aromatic feedstock for hydrocracking even at mild experimental conditions. It was also mentioned that this superacid could be used for oligomerization of cycloalkanes. Wen et al. [13] used solid super acid for hydrosomerisation of heptanes and hexadecane. The acidic functionality containing Mo and W has been shown to be superior to conventional amorphous catalysts with respects to acidity, selectivity and resistance to poison. Gates and co-workers [14,15] used polymer superacid resins for isomerisation and cracking of paraffins. Polymeric super acid are more feasible to produce olefins which leads to isomerisation followed by carbonium ion and hydride rearrangement. Imamura et al. [16-18] used brominated intermetallic compounds for isomerisation of pentane metal oxides. The following materials LaAl$_x$, CeAl$_x$, PrAl$_x$, ErAl$_x$, SmAl$_x$, and ThAl$_x$ were used for formation of intermetallics. Hattori et al. [19] prepared various types solid superacid by treating metal oxides with NH$_3$, FSO$_3$H, SbCl$_5$, SbF$_3$, and FSO$_3$H-SbF$_3$. The author observed that SbF$_3$ was better among all superacid for paraffins conversion. Even high conversion could be achieved at lower reaction temperature.

In this present work phosphomolybdic and phosphotungstic acids were prepared and their residue hydrocracking activities were
Experimental
Catalyst preparation

Three acidic catalysts phosphomolybdic acid, phosphotungstic acid and molybdenum-antimony fluoride superacid were used in this work. For the preparation of phosphomolybdic catalyst, MoO₃ was prepared first by heating of ammonium heptamolydbdate tetrahydrate (AHM) in SS tubular reactor at 450°C in presence of air for four hours. Molybdenum oxide was mixed with phosphoric acid and water in round bottle flask. The mixture was heated up to 4 hours and then filtered. During heating, the mixture becomes milky solution and then it changes to yellow with increasing temperature. The filtrate solution was boiled at 110°C and then cooled down so that crystallisation took place. The deep yellow crystals were obtained after drying in vacuum oven.

For preparation of phosphotungstic acid, Na₂WO₄·2H₂O was mixed with phosphoric acid and water in a round bottle flask. The mixture was heated. The acidification took place by addition of HCl. On the increasing temperature, the mixture colour changes to greyish colour. The mixture was heated up to 3 hours and then filtered. The filtrate solution was boiled at 110°C and then cooled down so that crystallisation takes place. The deep yellow-green crystals were obtained after drying in vacuum oven.

Mo based SbF₅ super acid catalyst was prepared in high pressure and high temperature reactor. Solution of ammonium heptamolybdiate was mixed with of SbF₅. The mixture was taken in a batch reactor and the reactor was pressurised by nitrogen. The mixture was heated to 180°C for 90 minutes. The reactor was cooled down and mixture was filtered with glass-wool. Flow diagram for the synthesis of three acid catalysts is described in Figure 1. The above prepared catalysts, phosphomolybdic, phosphotungstic and molybdenum-antimony fluoride acids are designated as H₃PMo, H₃PW and MoSbF respectively.

Catalyst activity test

The catalyst was tested in a high pressure and high temperature batch reactor. Before actual test run, the catalyst was sulphided in-situ. For this, the catalyst (aqueous solution) was taken with 200gm of feed which has very high concentration of sulphur. The reactor vessel was sealed properly and checked for leakage. The reactor vessel was then purged two/three times with hydrogen gas, so that there was no air left inside the reactor. An appropriate amount of hydrogen was added into the reactor so that the final pressure can reached to 100 kg/cm² at reaction temperature. Heating was started from room temperature to 350°C at the rate of 3°C/min. The sulphidation was performed in presence of high sulphur feed for 30 minutes.

After completion of sulphidation, the reaction temperature was increased to 410°C at the rate of 3°C/min. Stirring was started when temperature reached the set point (reaction temperature) and the time was noted as the beginning of the reaction. The experimental conditions for batch reactor are: reaction temperature, 410°C; reaction pressure, 100 cm²/kg; total reaction time, 4 h and stirring rate, 750 rpm. After the reaction liquid products were then separated from solid material. The residue conversion for this study was calculated by using the following equation:

\[ \text{Residue Conversion} = \frac{(550°C \text{ in feed} - 550°C \text{ in product})}{(550°C \text{ in feed})} \times 100 \]

Analysis of feed and products

Feed and hydrotreated liquid products were characterised by various techniques like, metal content using ICP-AES (Leeman Model DRE, PS-3000UV), sulphur content with Oxford sulfur analyser (Lab-X 3500) and CHNS analysis using Elementar Vario Micro CHNS analyser. ASTM D-4124-09 was used for SARA analysis. Coke was extracted from solid material by soxhlet method using toluene as solvent. Sulphur distribution of the liquid products was also analysed by GC using FFPD as sulphur specific detector. UV (model Shidamazu-2600) and FT-IR (model Nicolet-87000) techniques were also used to analyse the liquid products. These two techniques were also used to characterise the solid coke and catalyst respectively. XRD and TGA (model Perkin Elmer - 4000) were used to characterise the solid coke. TGA analysis was performed in the flow of air by heating the catalyst sample from room temperature to 900°C at the rate of 10°C/min. Product distribution of hydrotreated liquid was measured by TGA analysis. The details experiment procedure was given elsewhere [20,21].

Results and Discussion
Catalyst characterization

Thermal stability of two catalysts was measured by TGA and the results are presented in Figure 2. TGA curves show two distinctive characteristic of these two catalysts. Initial weight loss of H₃PMo catalyst is due to the water loss and around 22 wt% of weight loss is observed. It is worth to mention that total water was not removed during crystallization of this catalyst. After initial weight loss, the catalyst shows a stable form up to around 775°C temperature. Above this temperature, sharp weight loss of this catalyst is noticed. However,
the catalyst having tungsten shows stability with respect to temperature. Only around 4 wt% of weight loss is observed. Thermal stability of both molybdenum and tungsten based heteropolyacids were studied by Okuhara et al. [22]. The presence of two types of water- crystallization water and constitutional water was reported. The crystallization water is lost at lower temperature below 200°C whereas for the removal of constitutional water requires higher temperature. It was also reported that constitutional water is strongly attached with tungsten heteropolyacid and removal of it requires much higher temperature. Very minor loss of water during heating of phosphotungstic acid was also observed by other [6]. Overall TGA results show that phosphotungstic acid is thermally very stable compared with that of phosphomolybdic acid. Therefore no catalyst degradation or rearrangement is expected during actual hydroprocessing reaction conditions.

To characterize functional groups present in catalysts, Fourier transform infra red (FT-IR) spectroscopy was used. Both H3PMo and H3PW catalysts show very different FT-IR transmittance as shown in Figure 3. IR spectrogram of H3PMo catalyst reveals OH stretching and OH bending frequencies at around 2900 and 1415 cm\(^{-1}\) respectively. However, H3PW shows four absorption peaks of P-O, W-O, W-O-W (on plane) and W-O-W (out plane) at 1080, 981, 888 and 806 cm\(^{-1}\) respectively. These are characteristics peaks for phosphotungstic acid [23].

**Hydroprocessing activities**

Hydro-processing activities like hydro-desulfurization (HDS), hydro-demetalization (HDM), and asphaltene conversion (HDAs) of the prepared catalysts have been performed in the batch reactor. Vacuum residue having 5.45 wt% sulphur and 305 wppm of metals was used as feed for this study. The detailed characteristics of this feed are given in Table 1. Table also shows that this feed is highly viscous material and contains very high amount of microcarbon residue. This microcarbon residue has very detrimental effect due to its very high coke formation tendency during hydroprocessing reaction. It could be very difficult to hydrocrack this residue by conventional supported catalyst. In Figure 4, HDS, HDM and HDAs of three catalysts have been compared. The catalyst, phosphotungstic acid, gives the highest HDM and HDAs activities. Though the HDM and HDAs activities of H3PMo catalyst are less but it shows the slightly higher HDS activity.

Table 1 shows that feed contains very high percentage of metals mostly in the form of nickel and vanadium. These two metals in the feed are in the form of porphyrin and non porphyrin structure. The porphyrin structure is well characterised whereas non porphyrin structure is less characterised. The metals in non porphyrin structure may be associated with nitrogen, oxygen and sulphur in the defect centres of asphaltene molecule. The mechanism of metal removal from porphyrin ring by hydrogenation route (1).

![Figure 4](image)

**Figure 4:** Hydroprocessing activities of three acidic catalysts.

![Figure 5](image)

**Figure 5:** Mechanism of metals removal from porphyrin ring by hydrogenation route (1).

![Table 1](image)

**Table 1:** Characteristics of feed.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @15.6°C (g/mL)</td>
<td>1.05</td>
</tr>
<tr>
<td>(K_{cc}) @ 100°C (cSS)</td>
<td>25794</td>
</tr>
<tr>
<td>(\delta) @135°C (cSS)</td>
<td>1513</td>
</tr>
<tr>
<td>H/C (atomic)</td>
<td>0.07</td>
</tr>
<tr>
<td>S (wt %)</td>
<td>5.46</td>
</tr>
<tr>
<td>N (wt %)</td>
<td>0.87</td>
</tr>
<tr>
<td>Ni (wppm)</td>
<td>65.00</td>
</tr>
<tr>
<td>V (wppm)</td>
<td>240.00</td>
</tr>
<tr>
<td>Saturate (wt %)</td>
<td>8.89</td>
</tr>
<tr>
<td>Aromatic (wt %)</td>
<td>25.88</td>
</tr>
<tr>
<td>Resin (wt %)</td>
<td>43.25</td>
</tr>
<tr>
<td>Asphaltene (wt %)</td>
<td>21.98</td>
</tr>
<tr>
<td>MCR (wt %)</td>
<td>27.26</td>
</tr>
</tbody>
</table>
conversion. Though, the cracking activity in slurry phase reaction is mostly thermally controlled, but acidity and hydrogen functionally may facilitate this cracking activity. As it is mention that tungsten has comparatively high hydrogenation activity and therefore, this catalyst can easily hydrogenate aromatic rings before C-C bond cleavage. The product distributions obtained by these three catalysts have also been compared in Figure 7. This figure also shows that phosphotungstic acid produces higher percentage of lighter products like naphtha (<150ºC) and middle distillate (MD, 150-350ºC) in expense of residue and VGO. The productions of middle distillate and vacuum gas Oil (VGO) for H3PMo catalyst are almost same whereas middle distillate is higher than VGO in MoSbF catalyst. The handling of fluoride based MoSbF is quite difficult. Therefore, the use of tungsten containing heteropoly acid could be attractive option for hydrocracking of residue.

Characteristics of liquid products

During hydrocracking of vacuum residue at elevated temperature and pressure the large hydrocarbons are cracked to lighter hydrocarbons. The different properties of the liquid products are given in Table 2. Table shows that densities, kinematic viscosity, H/C ratio, of liquid products are very low compared with the feed. The MCR value of the feed is 27.26 wt% and it reduces to 4 wt% in H3PW catalyst. SARA analysis was also performed in liquid products. Table shows that resin content in liquid products obtained by catalysts H3PW and MoSbF is very low; whereas the saturate in H3PMo is high. The H/C ratio of liquid product also indicates the hydrogenation of the feed in the presence of acid catalysts. More hydrogenation of feed in H3PW is also noticed from the higher value of H/C.
UV visible spectrogram of liquid products is demonstrated in Figure 8. The bathochromic shift (red shift or spectra at longer wavelength) in UV spectra is an indication for the presence of aromatics. The red shift present in UV spectrogram reveals that W based heteropoly acid produce comparatively larger amount of aromatic compounds which is also observed in our SARA analysis.

The functional groups present in the liquid products are also measured by FT-IR and the results are given in Figure 9. The products of all catalysts show almost similar pattern indicating of having similar kinds of functional groups. In this figure, CH stretching for saturate of all catalysts show almost similar pattern indicating of having similar absorbance of aromatic groups which is also observed in our SARA analysis.

### Table 2: Characteristics of liquid products.

<table>
<thead>
<tr>
<th>Properties</th>
<th>H₃PMo</th>
<th>H₃PW</th>
<th>MoSbF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/mL) at 15.6°C</td>
<td>0.9334</td>
<td>0.884</td>
<td>0.9094</td>
</tr>
<tr>
<td>Kₗ (cSt) at 15.6°C</td>
<td>38.83</td>
<td>3.14</td>
<td>11.14</td>
</tr>
<tr>
<td>H/C (atomic)</td>
<td>1.54</td>
<td>1.59</td>
<td>1.53</td>
</tr>
<tr>
<td>Saturate (wt %)</td>
<td>32.93</td>
<td>13.46</td>
<td>14.68</td>
</tr>
<tr>
<td>Aromatic (wt %)</td>
<td>30.56</td>
<td>82.89</td>
<td>79.85</td>
</tr>
<tr>
<td>Resin (wt %)</td>
<td>32.34</td>
<td>1.46</td>
<td>2.64</td>
</tr>
<tr>
<td>Asphaltene (wt %)</td>
<td>4.17</td>
<td>2.19</td>
<td>2.83</td>
</tr>
<tr>
<td>MCR (wt %)</td>
<td>10.36</td>
<td>4.01</td>
<td>7.937</td>
</tr>
<tr>
<td>Refractive index (20°C)</td>
<td>1.6545</td>
<td>1.6495</td>
<td>1.6507</td>
</tr>
</tbody>
</table>

### Table 3: Characteristics of solid cokes.

<table>
<thead>
<tr>
<th>Properties</th>
<th>H₃PMo</th>
<th>H₃PW</th>
<th>MoSbF</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/C (atomic)</td>
<td>0.73</td>
<td>0.78</td>
<td>0.73</td>
</tr>
<tr>
<td>N (wt %)</td>
<td>1.74</td>
<td>1.39</td>
<td>1.49</td>
</tr>
<tr>
<td>S (wt %)</td>
<td>7.48</td>
<td>7.33</td>
<td>7.61</td>
</tr>
<tr>
<td>Ni (wppm)</td>
<td>643</td>
<td>441</td>
<td>498</td>
</tr>
<tr>
<td>V (wppm)</td>
<td>1318</td>
<td>833</td>
<td>799</td>
</tr>
</tbody>
</table>

Figure 9: FT-IR spectra of liquid products.

Figure 10: TGA curves of three solid cokes.
H$_3$PW is the hardest. The hardness property of a coke produced during hydrotreating reaction has been investigated in detailed by Beagon et al. [29] and Maity et al. [4,21]. As mentioned above that H$_3$PW catalyst is comparatively effective for deep residue cracking and it may also lead to deep polymerization reaction for the formation of coke. As a result, formation of condensed polyaromatic structure in coke is a possible explanation for the hardness property of this coke. If coke (H$_3$PW) is higher condensed, H/C ratio should be lower. However, the H/C in this coke is slightly higher than that of cokes produced by other two catalysts. It is observed above that thiophenic sulphur compounds are produced during cracking of residue in the presence of H$_3$PW catalyst. During cracking reaction, C-S bond (presence in branching of condensed aromatic rings) cleavage occurs and C-H bond is formed. This may be a possible explanation for having slightly higher H/C ratio.

The nature of coke formed during reaction is also characterised by solid UV. The coke in general is UV inactive and that why most of the radiations pass through the coke formed by H$_3$PW where as the radiations pass through the coke obtained by H$_3$PW where as the transmittance is shifted to higher wavelength region for the coke obtained by other two catalysts. Therefore, the results indicate that the hard coke transmits more UV ray.

The crystalline nature of coke and metals were examined by XRD analysis (Figure 12). In the MoSbF and H$_3$PMo, MoS$_2$ (2H) peak is observed at 20 = 14.44(002) (JCPDS data file 77-1716), and WO$_3$ peak appears at 36.91 (002) and 53.35 (222) (JCPDS data file 01-072-1465). The presence of graphitic carbon in all three coke samples is confirmed by 20 at 26.03 in the XRD diffractogram.

**Conclusion**

Heteropoly acid of phosphomolybdic, phosphotungstic and superacid of molybdenum antimony super acids are synthesized and their hydrotreating activities were studied on vacuum residue. Tungsten containing catalyst shows higher HDM, HDAs and residue conversion activities. It is believed that this is due to the higher hydrogenation activity of tungsten. HDS activity of phosphomolybdic acid is high. It is also observed that all three catalysts show considerable hydrotreating reaction at moderate operating conditions. It is also noticed from sulphur distribution of liquid product that due to C-S bond cleavage at branching of condensed aromatic rings, thiophenic sulphur compounds are formed. Moreover, phosphotungstic acid gives high percentage of aromatic products whereas the considerable amount of saturate hydrocarbons is produced by phosphomolybdic acid. The coke produced by H$_3$PW catalyst is hard in nature indicating that extensive polymerization reaction at reaction conditions. Higher H/C ratio indicates the deep hydrogenation of liquid products in presence of super acids. Phosphotungstic heteropoly acid could be useful for hydrotreating of residue instead of use superacid.

**References**

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