Activity of vanadium sulfide in the slurry phase hydroprocessing of vaccum residue

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Abstract: In this study the slurry phase hydrocracking (HCK) of vacuum residue (VR) was performed in an autoclave at 698K, 9.5MPa H_2 pressure in presence of V precursors. The characterization of catalysts was conducted by transmission electron microscopy (TEM) and X-ray absorption fine structure (XAFS) spectroscopy. It was revealed that the dispersed vanadium catalysts show a comparable catalytic activity with Mo catalysts based on the same mole amount loadings while the catalysts are less stable than Mo catalysts.

Keywords: vanadium sulfide, hydrocracking, dispersed catalyst.

1. Introduction

Since the conventional light crudes are getting limited, the upgrading technologies of heavy crudes have drawn much attention. For the upgrading of heavy oils hydrocracking has been considered as a promising process due to the capability of treating heteroatoms (S, N, V, Ni) and asphaltenes in heavy oils [1,2]. Differently from S and N species which can be converted to H_2S and NH_3 during the reaction, transition metals like V or Ni are usually transformed into metal sulfides causing precipitates particularly on the supported catalysts [2,3]. Therefore, dispersed catalysts, forming a slurry phase combined with heavy oils, are known to offer better activity and stability for the hydrocracking [4,5]. However, understanding about the phase transition and the properties of V or Ni precipitates are still lacking. It is thus the purpose of this study to investigate the influence of vanadium species on the slurry phase hydrocracking of vacuum residue.

2. Experimental

The hydrocracking (HCK) was performed in a 150mL autoclave batch reactor system in the presence of dispersed catalysts, produced by in-situ method from the precursors including molybdenum hexacarbonyl ($Mo(CO)_6$, Alfa Aesar, 98%) or vanadium acetylacetonate ($V(acac)_3$, Sigma-Aldrich, 97%). For the reaction, the 30g of VR was loaded in the autoclave with the catalyst precursors. After H_2 purging, the reaction was conducted at 693K, 9.5MPa H_2 pressure and 1000rpm. After reaction, the products were quantified by phase (gas, liquid, precipitate). Amount of asphaltenes and coke formation was measured by solvent extraction with n-heptane and toluene, respectively. Relative dispersibilities were determined by the amount of toluene insoluble products dispersed on 1-methyl naphthalene. The characterization was conducted with transmission electron microscopy (TEM) that model was JEOL JEM-2010 and conducted with X-ray absorption fine structure (XAFS) spectroscopy at beamline 8C and 10C of the Pohang accelerator laboratory.

3. Results and discussion

Figure 1 compares the reaction pressure profiles, relative dispersibilities and asphaltene conversions for the VR HCK in the presence of $Mo(CO)_6$ or $V(acac)_3$. In both cases pressure profiles show a decreasing trend, indicating a H_2 consumption via hydrocracking in the early stage of reaction. On the basis of the same weight loadings (Fig. 1A) a rebounding behavior was observed for V catalyst due to a loss of hydrocracking activity. In the case of the same moles of V or Mo in the VR HCK, the V catalyst shows a comparable HCK activity but with a slightly lower asphaltene conversion than the Mo catalyst (Fig. 1B). These results are related with the intrinsic hydrogenation activity and oil-dispersibility of V or Mo sulfides. Fig. 1A also compares the dispersibility of V and Mo catalysts, which reveals that the V catalyst is less stable than the

Mo catalyst. Figure 2 shows TEM images of the V and Mo catalyst which forms spherical and slab like particles, respectively in the size ranges of 5-10 nm. It can be noted that slab like particles offer better oil-dispersibility, leading to better accessibility towards asphaltenes in heavy oils.

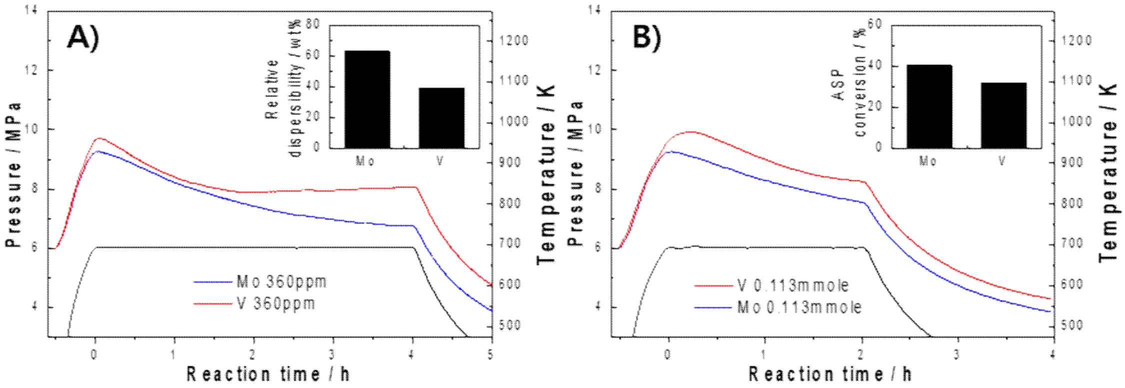

Figure 1. Comparisons of reaction pressure profiles, relative dispersibilities and asphaltene conversions of the dispersed catalysts.
A) Pressure profiles 360ppm metal basis and relative dispersibilities,
B) Pressure profiles 0.113mmole metal basis and asphaltene conversions.

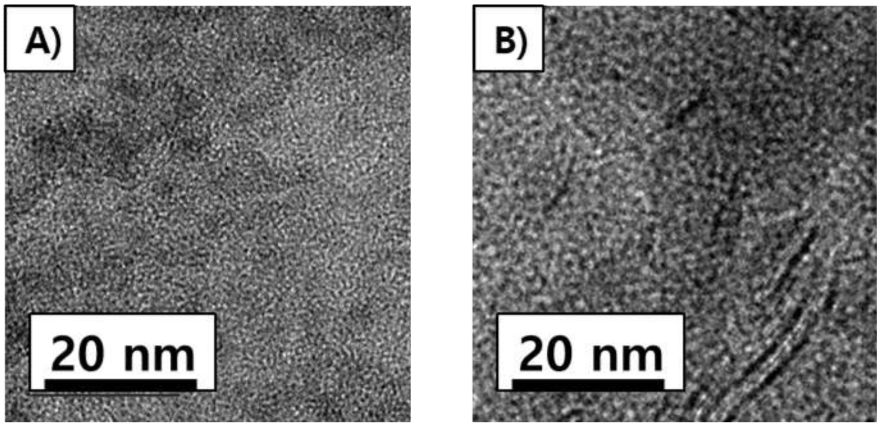

Figure 2 TEM images of the dispersed catalysts.
A) vanadium catalysts, B) molybdenum catalysts

4. Conclusions

Oil-soluble V precursors was applied to understand the phase transformation and catalytic activity of V species in the course of VR HCK. It was revealed that V forms spherically dispersed V sulfides, showing a comparable hydrocracking activity to that of MoS_2 catalysts on the basis of the same mole loadings, but with a low dispersibility.

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