Comparison of MoS_2 and WS_2 catalysts in the hydrocracking of vacuum residue

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Abstract: Catalytic activities and physical properties of Mo or W-based dispersed catalysts were compared for the hydrocracking (HCK) of vacuum residue (VR). Reaction tests were carried out in an autoclave at 692K for 2h, under hydrogen pressure of 6MPa at 353K. Structural properties of the Mo and W catalyst in the vacuum residue hydrocracking (VR HCK) were characterized by TEM and EXAFS measurements. Although the particle size of the WS_2 catalyst was formed larger than the MoS_2 catalyst in the course of VR HCK, the intrinsic HCK activity of the WS_2 catalyst was found higher than the MoS_2 catalyst based on TOF's.

Keywords: WS_2, MoS_2, hydrocracking, vacuum residue.

1. Introduction

Since the availability of conventional light crude oil is declining and being replaced by heavier feedstocks, the heavy-oil upgrading process has drawn much attention. The residue can be upgraded to light oil fractions either by thermal coking of catalytic hydrocracking processes [1-3]. The catalytic hydrocracking has shown superior performance in converting heavy oils into light oil fractions with high yield and quality over the conventional thermal processes. Among the catalytic hydrocracking processes a slurry phase hydrocracking using a dispersed catalyst system has shown advantages of better conversion and liquid yield [4,5]. This study has focused on the comparison of dispersed MoS_2 and WS_2 catalysts in terms of hydrocracking performance for vacuum residue and physical properties.

2. Experimental

The hydrocracking of vacuum residue was carried out using an 120 ml autoclave reactor at 692K for 2h and 9.5MPa H_2. For reaction tests, 30g of VR and 0.113mmol of catalyst precursor $Mo(CO)_6$ or $W(CO)_6$ were loaded. Unreacted asphaltenes in the reaction product were quantified by the precipitates with n-heptane-insolubles. TEM and EXAFS analysis were employed to identify structural properties of the catalysts. The EXAFS analysis was measured the Mo K-edge (19.999 keV) and W K-edge (10.207 keV) at the beamline 8C of the Pohang Light Source (PLS).

3. Results and discussion

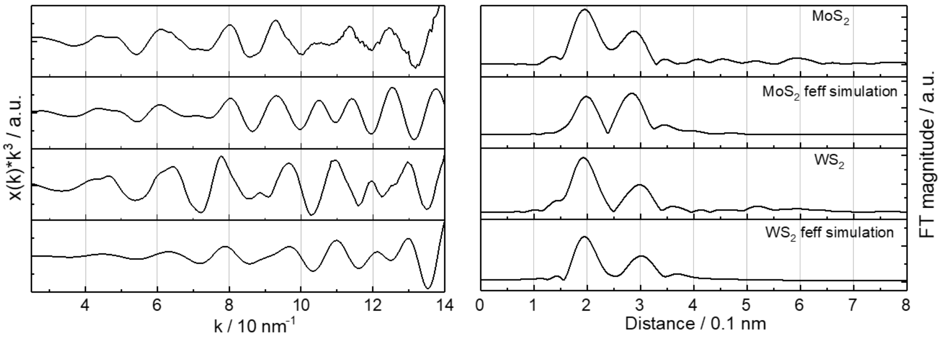

Figure 1. EXAFS spectra for the dispersed Mo and W catalysts

Figure 1 shows EXAFS spectra for the Mo and W catalysts collected after the VR HCK and confirms the formation of MoS_2 and WS_2, respectively. Figure 2 compares TEM images of the MoS_2 and WS_2

catalysts. It can be observed MoS_2 forms smaller particles of 9.8 nm in size than WS_2 with an average particle size 14.7 nm.

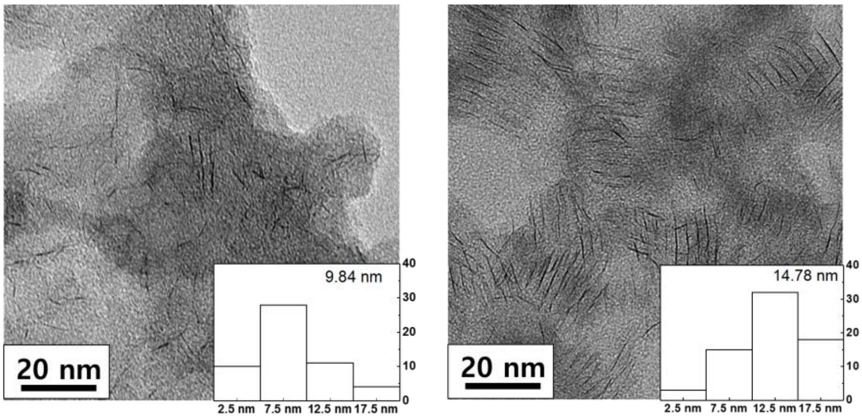

Figure 2. TEM images of MoS_2(left) and WS_2(right)

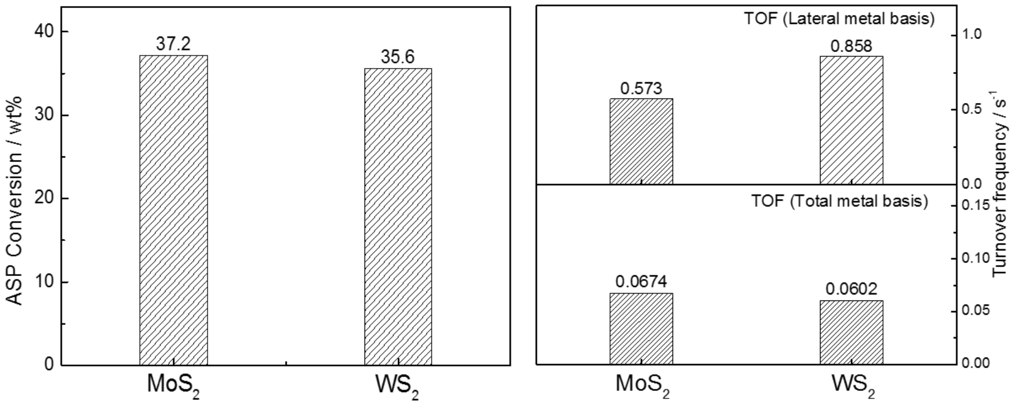

Figure 3. Comparison of asphaltene conversion and TOF over MoS_2, and WS_2

Figure 3 compares asphaltene conversions of VR HCK and TOF based on H_2 consumption rate per total or lateral metal site number. The WS_2 catalyst exhibited a lower asphaltene conversion and H_2-TOF based on total amount of metal loadings, while the TOF based on the lateral metal sites was found higher for the WS_2 catalyst.

4. Conclusions

The structure and catalytic activity of oil-dispersible Mo and W catalysts was compared for VR HCK. It was observed that in both cases the phase was transformed into sulfides as an active hydrocracking catalyst. Although the intrinsic VR HCK activity was found higher for the WS_2 catalyst than the MoS_2 catalyst, the particle size of the WS_2 catalyst was formed larger than the MoS_2 catalyst in the course of VR HCK, which led to a lower activity of the WS_2 catalyst in asphaltene conversion. It is thus suggested that the preparation of nano-scaled WS_2 catalyst would be crucial for a potential VR HCK catalyst.

References

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