Structure and Activity of dispersed Co-MoS₂ catalysts for hydrocracking vacuum residue

Ki-Duk Kim* and Yong-Kul Lee* *

*Laboratory of Advanced Catalysis for Energy and Environment, Department of Chemical Engineering, Dankook University, 152 Jukjeonro, Yongin 16890, South Korea
*Corresponding author: +82-31-8021-7216, yolee@dankook.ac.kr

Abstract: Nano-sized MoS₂ and Co-MoS₂ catalysts were synthesized by a ligand stabilization method and applied for hydrocracking (HCK) of vacuum residue (VR). The reaction was conducted at 10MPa H₂ and 693K for 2h in an autoclave reactor with catalysts of 0.113 mmol Mo. Characterizations made by TEM and EXAFS spectroscopy revealed that the MoS₂ phase of less than 10 nm in length became unstable in the course of the HCK. The introduction of Co could maintain the stability during the HCK of VR, with enhancing the HDS and HDN activity.

Keywords: MoS₂, CoMo, vacuum residue, hydrocracking, EXAFS.

1. Introduction

Recent increase of demand in light oil has spurred research in heavy-oil upgrading technologies. Among the heavy oils like petroleum residue and bitumen, vacuum residue (VR) occupying a half of heavier crude oil, has been a target to be upgraded into middle distillates. Slurry phase hydrocracking in the presence of unsupported MoS₂ catalysts is one of the most promising processes with high conversion rate of heavy oil to distillates [1-7]. The catalyst precursor can be a water-soluble salt, oil-soluble metal complex or a finely powdered solid. In the case of precursors oil-soluble catalyst was found superior to water-soluble precursors with a better dispersion and higher activity. In particular, the unsupported MoS₂ catalysts show superior activity and stability over the supported catalyst system for VR HCK [1-3].

2. Experimental

The MoS₂ and Co-MoS₂ catalysts were synthesized by a ligand stabilization method using trioctylphosphine oxide (TOPO) as a coordinating agent. As-prepared samples for all cases were characterized by transmission electron microscopy (TEM). The average particle size and standard deviation were measured and calculated from TEM image over 100 particles per sample. The X-ray absorption (XAS) spectra at the Mo K-edge (19.9999 keV) of reference and nanoparticle samples were recorded in the energy range from 4 to 40 keV at beamlines, 8C of the Pohang Light Source (PLS).

In order to evaluate the catalytic reactivity, different sets of experiments were performed at a 100mL autoclave, in which 30g of VR and 0.186g of catalyst (0.113mmol metal) were loaded. After purging the reactor was heated to 353K and simultaneously pressurized to 6MPa with H₂. The pressure reached to 10MPa upon the increase of temperature, and then the reaction was maintained for 2-4h.

3. Results and discussion

Figure 1 shows the TEM image for the fresh and spent MoS₂ and Co-MoS₂ catalysts. The MoS₂ catalyst was observed to grow in the particle size with the number of reactions from 6.5 nm in the first run to 11 nm after 3rd run. In contrast, the introduction of Co to the MoS₂, the catalyst maintained the morphology, demonstrating a beneficial role of Co-doping in the dispersion stability of MoS₂ nanoparticles.

Figure 2 shows the HDS and HDN activity of Co-MoS₂ for the hydrocracking of vacuum residue at 673K and 10.0 MPa. Co-MoS₂ catalyst was obviously superior both in the HDS and HDN over MoS₂ catalyst, again due to the promoting effect of Co. Moreover H/C ratio was further increased for the case of Co-MoS₂. Thus it can be suggested that the Co-doping could enhance both hydrocracking and hydrotreating activity via promoting hydrogenation activity for MoS₂ catalyst.
4. Conclusions

The nano-sized MoS$_2$ and Co-MoS$_2$ catalysts were well synthesized by a liquid phase sulfidation method in the presence of Mo(CO)$_6$, elemental sulfur, and TOPO. The EXAFS and TEM analysis suggested that high hydrogenation activity and dispersion stability of Co-MoS$_2$ catalysts contributed to the better activity for VR HCK than unpromoted MoS$_2$ catalyst.

References