Structure and Activity of dispersed Co-MoS_2 catalysts for hydrocracking vacuum residue

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Abstract: Nano-sized MoS_2 and Co-MoS_2 catalysts were synthesized by a ligand stabilization method and applied for hydrocracking (HCK) of vacuum reside (VR). The reaction was conducted at 10MPa H_2 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 MoS_2 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: MoS_2, 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 MoS_2 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 MoS_2 catalysts shows superior activity and stability over the supported catalyst system for VR HCK [1-3].

2. Experimental

The MoS_2 and Co-MoS_2 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 H_2. 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 MoS_2 and Co-MoS_2 catalysts. The MoS_2, 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 MoS_2, the catalyst maintained the morphology, demonstrating a beneficial role of Co-doping in the dispersion stability of MoS_2 nanoparticles.

Figure 2 shows the HDS and HDN activity of Co-MoS_2 for the hydrocracking of vacuum residue at 673K and 10.0 MPa. Co-MoS_2 catalyst was obviously superior both in the HDS and HDN over MoS_2 catalyst, again due to the promoting effect of Co. Moreover H/C ratio was further increased for the case of Co-MoS_2. Thus it can be suggested that the Co-doping could enhance both hydrocracking and hydrotreating activity via promoting hydrogenation activity for MoS_2 catalyst.

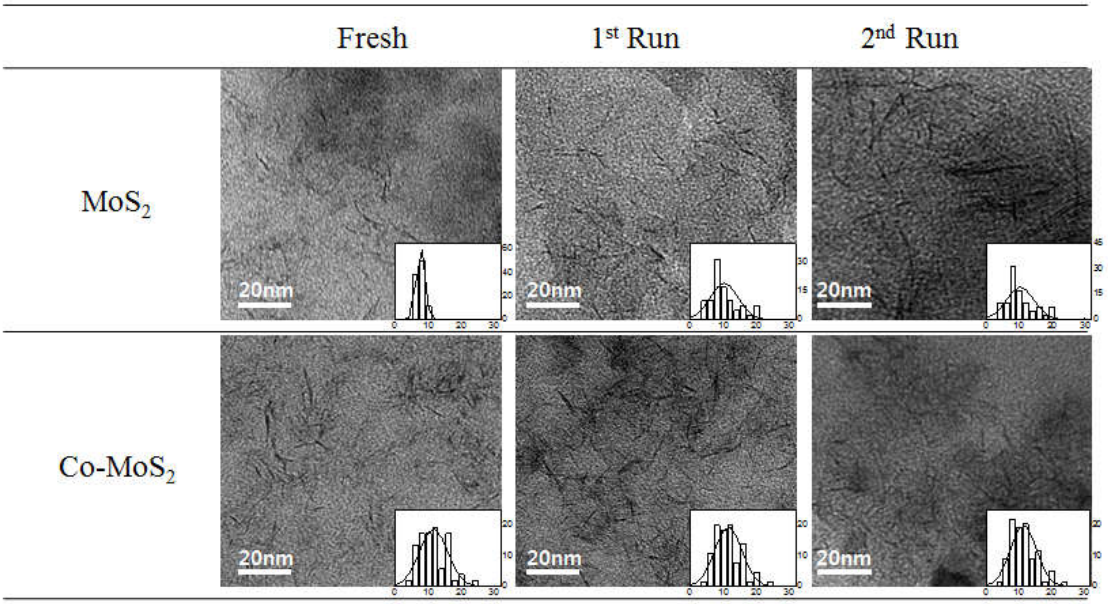

Figure 1. TEM images of fresh and spent MoS_2, Co-MoS_2 catalysts.

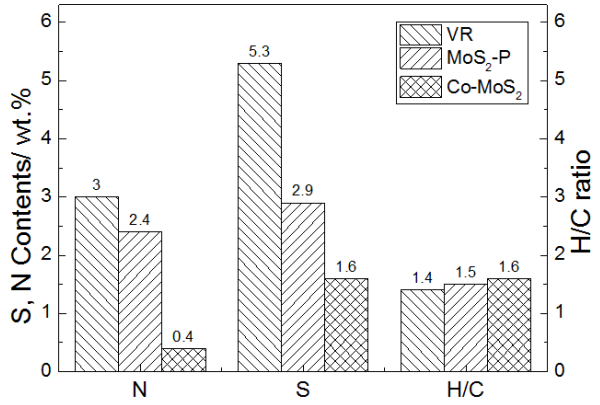

Figure 2. HDS and HDN results in the course of VR HCK over Co-MoS_2 nanoparticles.

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

1. S.-H. Kim, K.-D. Kim, Y.-K. Lee, J. Catal. 347 (2017) 127.
2. S.-H. Kim, K.-D. Kim, Y.-K. Lee, Chem. Eng. J. 314 (2017) 1.
3. P. Danial-Fortain, T. Gauthier, I. Merdrignac, H. Budzinski, Catal. Today, 150 (2010) 255.
4. G. Bellussi, G. Rispoli, A. Landoni, R. Millini, D. Molinari, E. Montanari, D. Moscotti, P. Pollesel, J. Catal. 308 (2013) 189.
5. A.I. d'Aquino, S.J. Danforth, T.R. Clinkingbeard, B. Ilic, L. Pullan, M.A. Reynolds, B.D. Murray, M.E. Bussell, J. Catal. 335 (2016) 204.
6. J.N.D. de Leon, T.A. Zepeda, G. Alonso-Nunez, D.H. Galvan, B. Pawelec, S., J. Catal. 321 (2015) 51.
7. M.S. Rana, V. Samano, J. Ancheyta, J.A.I. Diaz, Fuel, 86 (2007) 1216.