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# Beneficial roles of carbon black additives in slurry phase hydrocracking of vacuum residue

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ABSTRACT

Effects of carbon black (CB) additives with dispersed $MoS_2$ catalysts (d-$MoS_2$) on the slurry phase hydrocracking (HCK) of vacuum residue (VR) were studied in an autoclave batch reactor at 693 K and 9.5 MPa $H_2$. For comparison, commercial NiMo catalysts supported on large and small pore volume $Al_2O_3$ (-LP, -SP) were also applied for the VR HCK. The structure of the catalysts was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and extended X-ray absorption fine structure (EXAFS). The dispersed $MoS_2$ (d-$MoS_2$) was observed to form nanosized single slabs of 8.4 nm, while in the presence of CB the particle size of the d-$MoS_2$-CB became even smaller (4.8 nm). A series of recycle runs of the VR HCK revealed high activity and stability of d-$MoS_2$-CB followed by d-$MoS_2$ > NiMo-LP > NiMo-SP. The kinetic analysis also demonstrated that the d-$MoS_2$-CB shows a high asphaltene conversion with minimizing coke formation.

## 1. Introduction

The heavy oil upgrading technology has been expected as a solution for the demand of middle distillates and for the decline in the supply of light crude oils in the near future [1]. The vacuum residue (VR) is the heaviest fraction in crude oils, and thus needs to be converted into light distillates by the upgrading technology. However, VR contains 10 ~ 30 % asphaltene species that are rich in polyaromatics and heteroatoms inducing coke formation upon reaction severity [2–6], causing many problems like deactivation of catalyst, reduction of liquid yield, and fouling of reactor internals and vessels [7–9]. Since conventional supported sulfides were observed highly vulnerable to coke formation [3,8,10–16], slurry phase hydrocracking (HCK) has been introduced by using dispersed catalysts to lessen coke deposit [1,17–19]. Slurry phase HCK processes adopt finely dispersed catalysts that are added to the feed as oil-soluble precursors, being in situ transformed into a catalytic active phase in an intermediate activation step [18,20–28]. For example, Bellussi et al. confirmed that oil-soluble Mo precursors form nano-sized single slab $MoS_2$ particles, which are well dispersed in oil phase for VR HCK [29,30]. Our previous studies also revealed that dispersed $MoS_2$ phase is formed in the early stage of reaction but the particle size appears to grow with the progress of VR HCK [31–33]. Moreover, the growth of particle size was found to occur with coke formation, suggesting that the unstable behavior of the dispersed catalysts can be related to the phase separation of the reaction media [33].

VR is known to easily form a mesophase, a pre-stage of coke formation, causing a phase separation at a high temperature condition, Bagheri et al. observed the in situ formation of mesophase at a high temperature and pressure in VR HCK over supported catalysts [34]. Studies of fine additives as dispersants of asphaltenes in heavy oils were reported [34–39] and confirmed that the mesophase becomes smaller, delaying the transformation into coke particularly in the presence of fine additives. Similarly, Gentzis et al. studied the effects of fine additives like carbon shoots, showing effective coke reduction via size controls of mesophase [38,40]. Moreover, the carbon additives have been used as catalyst supports in the residue hydrocracking for reducing the formation of coke [41,42]. For example, Li et al. reported that a carbon black can adsorb heavy hydrocarbons and promote hydrogen transfer over Ni or Fe catalysts [41]. Lee et al. used carbon materials as supports for Co or Mo catalysts in packed bed reactor [43,44]. Although the effects of carbon additives on coke reduction behavior were well established, a detailed study to elucidate the relation between dispersed catalysts and carbon additives is still lacking. This study thus has focused on the verification of carbon additives in the presence of dispersed $MoS_2$ catalysts for VR HCK.

## 2. Experimental

### 2.1. Materials

Vacuum residue (VR) was supplied from a refinery in Korea, and the specification was summarized in Table S1 of supplementary materials

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