Influence of active phase structure of CoMo/Al$_2$O$_3$ catalyst on the selectivity of hydrodesulfurization and hydrodearomatization

W. Chen *, X. Long, M. Li, H. Nie, D. Li

Research Institute of Petroleum Processing, SINOPEC, P.O. Box 914, Beijing 100083, PR China

ABSTRACT

The relationship between the morphology and the selectivity of the sulfide phase in the hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene (4,6-DMDBT) and hydrodearomatization (HDA) reaction of 1-methylnaphthalene (1-MN) was studied. The morphology of the CoMo catalyst was tuned by increasing the metal content and adding organic compounds. The concentration of CoMoS sites at the corners ($C(CoMoS_C)$ and edges $C(CoMoS_E)$) of the sulfide slabs were measured by X-ray photoelectron spectroscopy and high resolution transmission electron microscopy techniques. The corner and edge sites of the sulfide phase account for the direct desulfurization (DDS) and hydrogenation desulfurization (HYDS) routes in the HDS of 4,6-DMDBT, respectively. The hydrogen consumption analysis showed that the HYDS of 4,6-DMDBT and HDA of 1-MN both occur at the edge sites of the MoS$_2$ slabs. The HYDS route in 4,6-DMDBT HDS was more promoted than the 1-MN HDA reaction when the stacking was increased. The turnover frequency of the corner sites for the DDS reaction and edge sites for the HYDS and HDA reactions were correlated with the length and stacking of the sulfide phase. The results revealed how the selectivities of the DDS, HYDS and HDA reactions as well as the hydrogen consumption can be tuned by modifying the morphology of the sulfide phase.

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1. Introduction

Hydrodesulfurization (HDS) plays an important role in upgrading diesel fuel to an ultra-low sulfur level [1–3]. In the process, the hetero atoms (S, N) are removed over the HDS catalyst in the presence of high pressure hydrogen and a large quantity of hydrogen is continuously consumed by hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HDA) reactions [4]. Therefore, it is essential to reduce the hydrogen consumption in order to save cost and enhance the profits of the refinery. Dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are regarded as the most refractory molecules in the ultra-deep HDS of diesel [5]. The sulfur atoms are mainly removed through two pathways, named the direct desulfurization (DDS) and hydrogenation desulfurization routes (HYDS). In the DDS route, the sulfur is eliminated by direct scission of the C—S bonds whereas the prehydrogenation of the aromatic ring in the sulfur compounds is required in the HYDS route [1]. Obviously, the HYDS route consumes a higher amount of hydrogen than the DDS route. Besides

HDS reactions, the HDN and aromatics saturation reactions also consume hydrogen. Due to the difference in content, hydrogen consumption in the HDS of diesel is mainly dependent on the HDS and HDA reactions. In particular, the portion of refractory sulfur compounds and aromatics in the diesel feedstock exhibits an increasing trend since more fluid catalytic cracking (FCC) diesels fractions have to be blended and upgraded [6]. Therefore, tuning the selectivities of the catalyst in the HDS of refractory sulfur-containing compounds and HDA reactions is important for reducing hydrogen consumption.

The transformation of refractory sulfur compounds over HDS catalyst has been extensively studied in the literature [7–18]. In the removal of DBT, the DDS pathway is much more reactive than the HYDS route [19–26]. The ratio of the DDS and HYDS selectivities (S_{DDS}/S_{HYDS}) may vary in the range of 4:1–9:1 depending on the metal type and reaction conditions. When the methyl substitutions in the aromatic rings are located adjacent to the sulfur atom of DBT, the DDS route is remarkably inhibited due to steric hindrance whereas the HYDS route is only slightly affected [19–25]. Consequently, the HYDS route turns out to be important in the HDS of 4,6-DMDBT and the S_{DDS}/S_{HYDS} ratio can be decreased to 1.3:1–0.5:1. Regarding the reaction mechanism, it is generally accepted that the DDS reaction involves σ adsorption of the DBT molecule via the sulfur atom, whereas HYDS proceeds through π

adsorption of the reactant via the aromatic ring [23]. In the real feedstock, the presence of H_2S and aromatics affects the selectivity of DDS and HYDS due to their competitive adsorptions on the active sites [23,26–28]. The rate of the DDS route in the HDS of DBT and 4,6-DMDBT can be markedly decreased by H_2S whereas the HYDS pathway is less blocked [29]. Regarding the inhibition by aromatics, Kim et al. reported that 1- methylnaphthalene (1-MN) produced a more negative effect on the hydrogenation pathway than on the hydrogenolysis route in the HDS of 4,6-DMDBT [30]. Farag et al. reported that naphthalene had more impact on the HYDS than on the DDS route in the HDS of 4,6-DMDBT, leading to a slight increase of the S_{DDS}/S_{HYDS} selectivity [31]. Even though the impact of aromatics has been frequently studied, the selectivity ratio of HDS and HDA (S_{HDS}/S_{HDA}) has been less studied, particularly when the content of aromatics was high.

To better tune the S_{DDS}/S_{HYDS} and S_{HDS}/S_{HDA} selectivities in the HDS process, the structure and location of the active sites for specific reactions should be taken into consideration. The active phase in sulfide catalysts is present as small hexagonal MoS_2 or WS_2 slabs with the edges and corners decorated by the promoter atoms (Co or Ni) [1,8,16]. The real structure of the catalytic sites involved in hydrogenolysis and hydrogenation reactions has been heavily discussed for many years [1,7,8,16,32,33]. Topsøe et al. estimated the fraction of edge sites in the catalyst and pointed out that an increasing fraction of the atoms along the edges would be "corner atoms" as the MoS_2 particle size is decreased. The edges sites are more active for HDS than the corner atoms [34,35]. Massoth found that the sites at edges and corners may have different reactivity and suggested that the HDS reaction occurred at vacancies on corner sites and that the hydrogenation reaction took place at vacancies on edge sites [36]. In the "rim-edge" model developed by Daage and Chianelli, the unsupported MoS_2 particle was regarded as a stack of several disks in which the rim sites were located at the top and bottom disks and the edge sites was associated with the disks "sandwiched" between the top and bottom disks [37]. The model indicated that the sulfur hydrogenolysis occurred on both the rim and edge sites, whereas DBT hydrogenation was believed to occur exclusively on the rim sites. In recent years, the Topsøe group viewed a kind of metallic- like site (named BRIM site) in sulfide cluster in scanning tunneling microscopy (STM) images [32,38,39]. The BRIM sites are located adjacent to the edges and bind the sulfur-containing compounds and catalyze the hydrogenation reaction with the hydrogen activated at the neighboring edge sites on the MoS_2 and CoMoS structure [40,41]. The direct image of the adsorption of 4,6-DMDBT with STM at low temperatures showed that the adsorption onto sulfur vacancies on MoS_2 edges in the DDS route was strongly sterical inhibited and certain corner sites in the MoS_2 slab and the promoted CoMoS structures may directly facilitate the adsorption [41].

According to these arguments, different reactions may take place on specific position of the MoS_2 slabs. Therefore, the variation of the morphology of the MoS_2 slabs may alter the selectivity of the catalyst. Silva et al. tested the S_{HDS}/S_{HDA} selectivity in the HDS of DBT and hydrogenation of 1- MN (20 wt%) over a series of Mo/Al_2O_3 catalysts in the presence of isoquinoline [42]. It was found that the HDA activity was gradually increased whereas the HDS activity remained constant as the Mo loading in the catalyst increased. The HDA activity was related to the number of edge or edge + corner sites whereas the HDS was not related. Hensen et al. indicated that the selectivities for HDS and hydrogenation can be tuned by the morphology of MoS_2 phase and the choice of support. The high hydrogenation rate constant for a Mo/C catalyst was ascribed to the large number of corner sites [43]. Liu et al. [44] found the hydrogenation selectivity of a NiMo catalyst increased linearly with the stacking number. The high stacking degree of MoS_2 slabs was beneficial for the flat adsorption and reaction of DBT. Li et al.

reported that the morphology of MoS_2 slabs can be modified on different supports. The HDS selectivity in the hydrogenation of thiophene and 1-hexene correlated linearly with the length of the slab, indicating that the corner sites rather than the edge sites may favor hydrogenation [45].

These results indicate that the selectivity of hydrogenolysis and hydrogenation correlates with the morphology of the active sites, but the corresponding sites are still under debate. This inevitably causes ambiguity for tuning the S_{DDS}/S_{HYDS} and S_{HDS}/S_{HDA} selectivity in diesel upgrading. In order to clarify the effect of the morphology structure on the selectivity of HDS catalyst in HDS and HDA reactions, two solutions were used to in the present work modify the morphology of the sulfide phase including varying the metal contents [42,44,46–48] and introducing ethylene glycol (GL) [49] and citric acid (CA) [50–56]. The S_{DDS}/S_{HYDS} and S_{HDS}/S_{HDA} selectivities were evaluated in the simultaneous HDS of 4,6-DMDBT and HDA of 1-MN. The relationship between the structure and the catalytic functions was studied.

2. Experimental

2.1. Catalyst preparation

A series of CoMo catalysts with different metal loadings was prepared by the classical incipient wetness impregnation method. The basic cobalt carbonate and molybdenum oxide precursors were sequentially added to the proper amount of phosphoric acid solution in the presence of ethylene glycol (abbreviated as GL). The solution was heated under stirring until the precursors were completely dissolved. Afterwards, the solution was mixed with extruded alumina under quick shaking. The impregnated catalyst was dried at 120 °C for 3 h. The obtained oxidic catalysts with different metal contents were nominated as CoMoGL-1, CoMoGL-2, CoMoGL-3 and CoMoGL-4, respectively. Following the same preparation procedure, catalysts without addition of chelating agent and containing citric acid (CA) were prepared and named CoMoP and CoMoCA, respectively.

The contents of the metal components in the catalysts are displayed in Table 1. In order to calculate the volume concentration of the metals in the catalyst, around 5 mL of support with 40–60 mesh particle size was packed in a 5 mL cylinder and the volume of the support was determined after sufficient densification of the particles by knocking the cylinder. The packing density of the support was calculated by dividing its weight by the measured volume. The packing density of the support ($d_{Al_2O_3}$, g/mL) was the average value of three measurements. The densities of all catalysts were also measured by the same method.

The volume molar concentration of Mo (C(Mo), mol/L) and Co (C(Co), mol/L) atoms was determined by the equation:

$$C(\text{Mo}) = \frac{[\text{MoO}_3]}{M_{\text{MoO}_3}} \div \frac{[\text{Al}_2\text{O}_3]}{d_{\text{Al}_2\text{O}_3}} \times 1000, \quad C(\text{Co}) = \frac{[\text{CoO}]}{M_{\text{CoO}}} \div \frac{[\text{Al}_2\text{O}_3]}{d_{\text{Al}_2\text{O}_3}} \times 1000 \qquad (1)$$

where [MoO_3], [CoO] and [Al_2O_3] are the weight contents of MoO_3, CoO and Al_2O_3 in the catalysts, M_{MoO_3} and M_{CoO} are the molar mass of MoO_3 and CoO. The detailed data are listed in Table 1.

2.2. Catalyst characterization

2.2.1. Preparation of sulfide catalyst

Prior to the XPS analysis, the sulfide catalyst was prepared under H_2S/H_2 atmosphere. The oxidic catalyst (40–60 mesh) was installed in the homemade sulfidation equipment. The sulfidation was carried out at 400 °C for 3 h (ramp rate: 10 °C/min) under H_2S (2%)/H_2 gas. N_2 gas was switched to flush the sulfide sample for 30 min when the temperature was decreased to 120 °C. After the temperature was decreased to room temperature, the sample was sealed