Study on effects of different sulfidation processes of commercial hydrotreating catalysts

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Abstract: In this study, a commercial hydrotreating catalyst which contains organic chelating agent is selected. The generation of the sulfurization phases and the activities of the catalysts in different sulfurization processes are investigated by using fixed bed reactors and CO adsorption in-situ FTIR characterization. The results show that the higher initial temperature of sulfurization (> 200℃) leads to the decreasing of catalysts activities, which due to less generation of high activity CoMoS phases at the higher sulfurization initial temperature.

Keywords: Hydrotreating catalyst, organic chelating agents, sulfurization.

1. Introduction

To produce clean diesel fuel which sulfur contents <10 ng/μl, the activities of commercial catalysts, which are key factors in hydrotreatment, must be improved. Adding organic chelating agents, such as nitrilotriacetic acid, citric acid, glycol and ethylene diamine tetraacetic acid (EDTA) is a useful method to improve the activity of commercial hydrotreating catalyst. Several works have confirmed it [1-3]. These novel catalysts generate a large amount of highly active Co(Ni)-Mo-S type II active phases during sulfurization processes, thereby the intrinsic activities of the catalysts are increased. However, unlike sulfurization processes of conventional catalysts, catalysts containing organic chelating agents are accompanied by the decomposition of the organics and exothermic reaction during the sulfurization process while the sulfided active phases are generating. Therefore, it is necessary to study the effect of sulfurization process during the catalyst sulfurization.

In this study, a Co-Mo commercial hydrotreating catalyst which contains EDTA as chelating agents was selected. The effects of different sulfurization initial temperature on the generation of active phases and catalysts activities were investigated.

2. Experimental

Hydrotreating catalysts: developed by Fushun research institute of petroleum and petrochemicals, Sinopec. Sulfurization oil: aviation kerosene containing 1.4 wt% CS_2. Feedstocks: straight-run distillate diesel which contain sulfur 1.4 wt%.

The fixed bed reactors were used for catalysts sulfurization and activies evaluation. 10 mL (18-20 mesh) catalysts were loaded in the reactor tube. Activity evaluation tests conditions: liquid hourly space velocity was 2.0 h^{-1}, hydrogen oil volume ratio was 300, reaction temperature was 370℃, and the reaction pressure was 5.0 MPa. For inestigating the effects of sulfurization reaction processes, the initial temperature of sulfurization was 100, 150, 200, 250, 300, 350, 400℃, respectively and the ending temperature was 400℃. The sulfurization holding time was 8h.

3. Results and discussion

The activities of seven catalysts which are sulfurized in dufferent sulfurization initial temperature are evaluated. The results are shown in figure 1(a). It shows that the hydrodesulfurization activites of the sulfided catalysts maintain stability when the sulfurization initial temperatures increase from 100℃ to 150℃. However, when the sulfurization initial temperature is up to 200℃, the hydrodesulfurization activites of the sulfided catalysts begin to decrease with the temperature increasing. The highest hydrodesulfurization conversion rate is 98.95%.

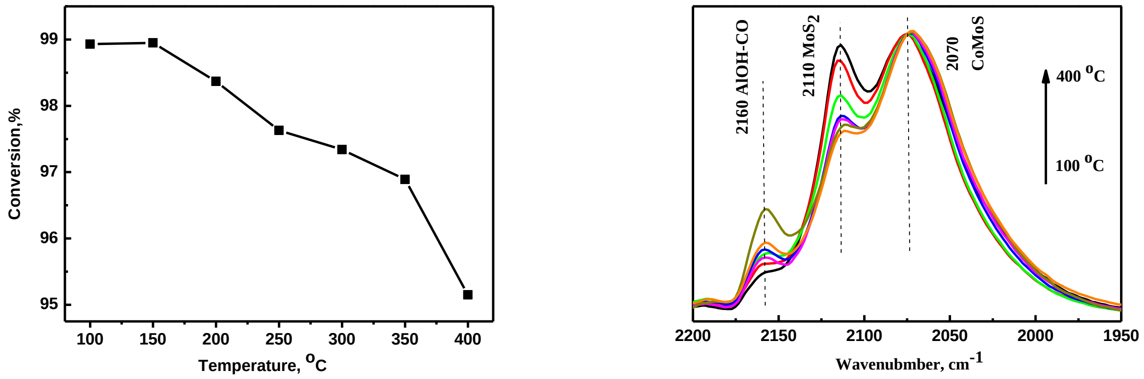

Figure 1. (a) Desulfurization activities of catalysts in different sulfidation beginning temperatures. (b) CO adsorption in-situ FTIR spectra of catalysts in different sulfidation beginning temperatures.

Figure 1(b) illustrates CO adsorption in-situ FTIR spectra of catalysts in different the initial temperature of sulfurization. Three vibration bands representing different CO adsorption position are detected at 2157, 2110, 2070 cm^{-1}. According to the researches of Travert and Dujardin et al. [4, 5], the band which appears at 2157 cm^{-1} is due to CO adsorption on the Al_2O_3 support and correspond to coordinationon hydrogen bonding with the surface hydroxyl groups. The band appearance at 2075 cm^{-1} correlates with the formation of the Co-Mo-S phase while the band at 2110 cm^{-1} appears to be related to the MoS_2 phase. The bands of 2110 and 2070 cm^{-1} are fixed and the proportions of the highly active Co-Mo-S phase and the less active MoS_2 phase are calculated. The results are listed in table 1.

Table 1. CoMoS/MoS_2 ratio of catalysts in different sulfurization initial temperature

Sulfurization beginning temperature, ℃	100	150	200	250	300	350	400
$Area_{CoMoS}/Area_{MoS2}$	12.35	12.41	11.31	11.29	7.42	4.42	3.22

Table 1 shows that the CoMoS/MoS_2 ratio are nearly identical (12.4) when the initial temperatures of sulfurization are 100℃ and 150℃. When the initial temperature of sulfurization is increased to 200℃ or higher, the CoMoS/MoS_2 ratio decreases as the temperature rises. The decreasing in the CoMoS/MoS_2 ratio corresponds to the activites decreasing of the catalysts and could be considered as the main reason for the change in the catalyst activity.

4. Conclusions

The activities of commercial hydrotreating catalysts containing organic chelating agents are higher at lower initial sulfurization temperatures (<200℃). It is due to more highly activity CoMoS phase generation at lower initial sulfurization temperature. This study helps to improve the application of commercial hydrotreating catalysts containing organic chelating agents.

References

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