Novel ex-situ presulfurization technology developed for hydrotreating process

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Abstract: Dalian Research Institute of Petroleum and Petrochemicals of SINOPEC successfully developed an innovative ex-situ presulfurization technology (EPRES). The technology involves sulfurizing the metal oxides of hydrotreating catalyst to the corresponding metal oxy-sulfides outside the reactor, by first dispersing an organo-nitrogen containing substance onto the oxide catalyst, and then introducing sulfur together with a specific organic solvent, and followed optimizing the heat treatment of the corresponding catalyst.
Keywords: Ex-situ, Presulfurization, Hydrotreating.

1. Introduction

For selective removal of sulfur and nitrogen compounds, hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are the two important reactions in hydrotreating of heavy oil feedstock containing high concentrations of sulfur and nitrogen compounds in refineries. The hydrotreating catalysts are commonly sulfide Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3. Presulfurization is an essential process for activation of a hydrotreating catalyst in the oxidic form. The conventional process, i.e., in situ presulfurization (IPRES), is used to sulfurize the pre-loaded catalyst in a reactor by introducing a sulfurizing agent.Onthe contrary, ex situ presulfurization (EPRES) is the process in which the catalyst is sulfurized or partially sulfurized before loading the catalyst into reactor. Compared with in situ sulfurization, ex situ presulfurization takes much shorter period of treating time, hence significantly increases production efficiency.

2. Experimental

The technology involves sulfurizing the metal oxides of hydrotreating catalyst to the corresponding metal oxy-sulfides outside the reactor, by first dispersing an organo-nitrogen containing substance onto the oxide catalyst, and then introducing sulfur together with a specific organic solvent, and followed optimizing the heat treatment of the corresponding catalyst. The function of the introduced organonitrogen compound is to enhance the diffusion of sulfur into catalyst pores and therefore accomplish uniform sulfur dispersion. Moreover, the presence of organo-nitrogen substance can restrain the reaction of sulfur with hydrogen-containing compound to form H_2S, not only increases the sulfur utilization efficiency but also reduces the environmental impact of H_2S product. The adopted multiple step heat treatment can optimize various state of the intermediate compound $MeO_{(x-y)}S_y$, leading to a reduction in the release of concentrated exothermic heat during start-up procedure and rather structurally amorphous metal oxy-sulfide species.

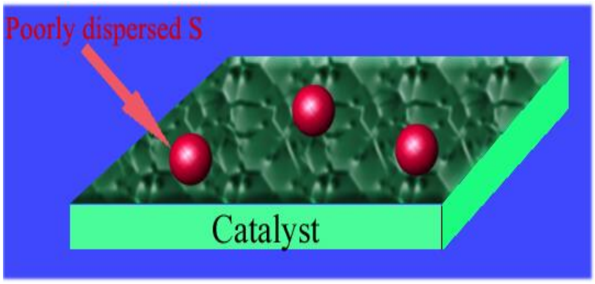
3. Results and discussion

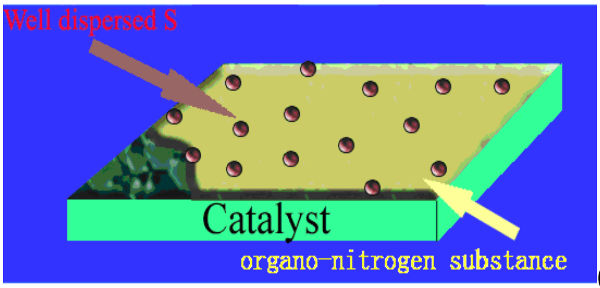
We studied our EPRES catalyst with respect to the in situ presulfurization (IPRES) counterpart, to clarify the difference of their structures, the dispersion and the state of the active surface NiMoS/MoS_2 species.

The presulfurized EPRES catalysts and the IPRES counterpart are systematically characterized by TEM, XRD and XPS, and correlated with their catalytic activities. The exothermic effect of the EPRES process is verified by HPDTA study. Remarkable features of the present EPRES catalyst are recognized: higher content of active surface NiMoS/MoS_2 species, less fraction of metallic Ni, and more uniform dispersion of surface sulfide species, which are the key factors accounting for the observed better HDS and HDN activities. The current technology comprises the following characters: controlling the degree of sulfurization with appropriate thermo-treatment, and eliminating the concentrative exothermic effect with optimized sulfurizing agent(s) and better introducing manner. The process has been proved to shorten the start-up procedure efficiently in pilot plant and commercial application, being more economical and environmentally friendly.

At certain temperature the sulfurizing agent starts reaction with metal oxide precursor to generate the oxy-sulfide and to release water. The oxy-sulfide decomposes at higher temperatures accompanying the release of H_2O and SO_2, which in turn decreases the sulfur content in the EPRES catalyst. There is remarkable heat release (exothermic effect) during the presulfurization and activation processes. Presulfurization at higher temperatures can suppress the exothermic effect meanwhile the over-heating results in low catalyst activity. The effectiveness of presulfurization is closely related to the formation of oxy-sulfide species, and its decomposition is unfavorable for the ultimate activity. Both the preparation parameters and the operating conditions can affect the exothermic behaviour and surface property of the EPRES catalyst. The investigation on the ex situ presulfurization of the single metal based (W, Mo, Ni or Co) samples revealed that the formation of oxy-sulfide species and the involved exothermic effect are closely related to the kind of metal element and the specific treatment applied, which is helpful for understanding the nature of the multi-component EPRES catalysts.

Currently we are developing new generation of EPRES catalyst by controlling the morphology and facet structure of support material, enhancing dispersion of metal oxide capacity, improving reactivity of dispersed metal oxide species toward sulfurizing agent under mild conditions, and achieving the highest degree of sulfurization as possible. The new catalyst has superior catalytic efficiency yet lower production cost, suitable for the increasingly demanding of today's hydrotreating process and technology.



(a)


(b)

Figure 1. The illustration of sulfur dispersion on the catalyst (a) without and (b) with the organo-nitrogen substance.

4. Conclusions

The EPRES technology of FRIPP, SINOPEC has the following advantages: (1) Low cost of raw materials and simplified manufacturing process; (2) High degree of sulfurization of metal oxide components in catalyst; (3) High activity yet low concentrative exothermic effect of EPRES catalyst; (4) Free of N_2 protection during storage, transportation and loading of the catalyst; (5) Reduction of start-up procedure of hydrotreating unit; (6) Enhancement of process safety. More than 30 types of EPRES catalysts have been manufactured and used successfully in various industrial units with a total capacity of 36.7 million tons, and achieved remarkable economic benefit and social profit, being of great importance to enhance competition ability in hydroprocessing market in China.

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