Studies on pore structure modification of Al_2O_3-based catalyst for the selective hydrodesulfurization of fluid catalytic cracking gasoline

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Abstract: Co-Mo/γ-Al_2O_3 catalyst with modified pore structure was designed for the selective hydrodesulfurization of fluid catalytic cracking(FCC) gasoline. The catalyst support and catalyst were characterized by N_2 adsorption-desorption, temperature-programmed desorption of ammonia(NH_3-TPD), high-resolution transmission electron microscopy. Compared with unmodified catalyst, which had similar physicochemical properties with the modified catalyst except for the pore diameter, the modified catalyst with larger average pore diameter displayed increased HDS activity and selectivity.
Keywords: Co-Mo/γ-Al_2O_3 catalyst, selective hydrodesulfurization, larger pore structure catalyst.

1. Introduction

In order to reduce vehicle pollution, new restrictive regulations for sulfur content in vehicle gasoline have been adopted in both developed and developing countries. Fluid catalytic cracking(FCC) gasoline, accounting for about 70% in the total petrol pool, contributes more than 90% of sulfur[1]. Hydrodesulfurization is one of the most important processes for removing sulfur from FCC gasoline. However, the conventional HDS technique usually causes olefin saturation, which results in a serious loss in octane number. Therefore, selective hydrodesulfurization that can remove sulfur compounds with the lowest level of olefin saturation is highly desired.

In order to minimize the octane loss, many investigators have focused on exploring the nature of active, effect of supports, reaction mechanism, as well as new reactor technologies[2]. But the effect of pore structure was usually ignored. In recent studies, the pore structures have tightly attracted the attention of researchers. For example, the effects of the pore structure (based on SBA-15) on HDS performance have been studied[3], and it was concluded that both the pore size and the window size play an important role in the HDS activity. Liu et al.[4] found that the coprecipitation Ni-Mo/Al_2O_3 catalyst with a macroporous structure exhibited a superior durability for hydrodesulfurization of dibenzothiophene to other catalysts without macropores. However, to our knowledge, few researchers have investigated the effect of pore structure in the selective HDS of FCC gasoline.

In this study, a simple method to prepare Co-Mo/γ-Al_2O_3 catalyst with modified pore structure was described. In order to reveal the effects of pore structure of the catalyst in the selective HDS of FCC gasoline, we evaluated the activity and selectivity of the modified and unmodified catalyst in the HDS of FCC gasoline in a fixed-bed high-pressure micro-reactor.

2. Experimental (or Theoretical)

2.1. Support synthesis. The modified P1 alumina sample and unmodified P2 alumina sample were kneaded and extruded to produce three-lobed extrudates that then were dried in air for 1 day, heat treated at 120℃ for 4h and at 600℃ for 4h in air, respectively.

2.2. Catalyst Synthesis. Co-Mo/Al_2O_3 catalyst were prepared via the wetness impregnation method. P1-Co-Mo and P2-Co-Mo were obtained from P1 and P2, respectively.

2.3. Catalyst Characterization. The pore structure of the Al_2O_3 extrudates were measured using the N_2 adsorption-desorption method.

2.4. Catalytic tests. The catalytic performance was assessed in a continuous-flowing fixed-bed reactor.

3. Results and discussion

Table 1 shows the pore structure parameters of the modified and unmodified support. The average pore diameter of the modified support was much larger than that of the unmodified support, meanwhile the S_{BET} was not changed.

Table 1 Textural properties of the different suports

Sample	S_{BET} (m^2/g)	PV (cm^3/g)	Average pore size(nm)
P1	315.3	0.48	6.1
P2	327.6	0.70	8.6

The HDS reaction rate and selectivity are shown in Fig. 2 and Fig. 3. The catalytic performance indicates that larger average pore diameter may significantly enhanced the overall HDS reaction rate and selectivity.

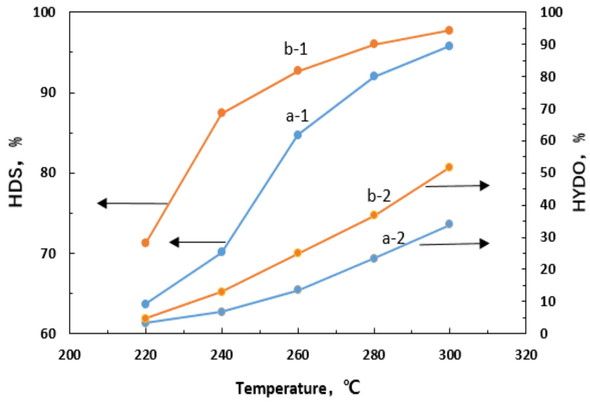

Fig. 2 Effect of temperature on HDS and HYDO activity of P1-Co-Mo and P2-Co-Mo with the heavy fraction of FCC gasoline as the feedstock under the conditions H2/oil volumetric ratio 300, total pressure 2Mpa, and LHSV $4.0h^{-1}$

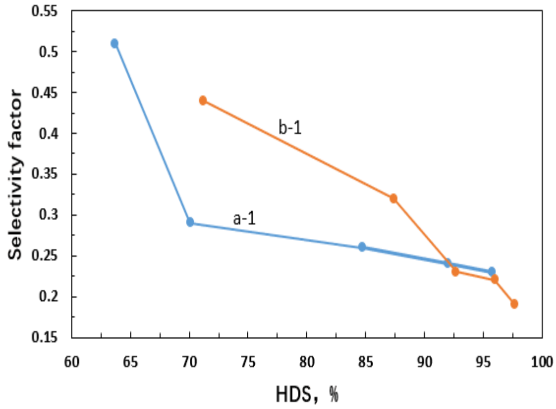

Fig. 3 HDS selectivity factor of P1-Co-Mo and P2-Co-Mo

4. Conclusions

The average pore diameter was important for the catalytic performance of $CoMoS/Al_2O_3$ catalysts in FCC gasoline HDS. The modified catalyst with larger average pore diameter enhanced HDS activity and selectivity.

References

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