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Selectivity enhancement of CoMoS catalysts supported on tri-modal porous Al_2O_3 for the hydrodesulfurization of fluid catalytic cracking gasoline

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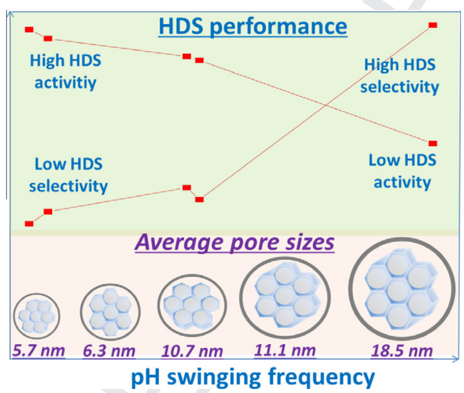
HIGHLIGHTS

- Catalyst prepared with macropore Al_2O_3 shows high HDS selectivity but low activity.
- Micro-, meso-pore Al_2O_3 possesses high HDS activity but low selectivity.
- Tri-pore distribution Al_2O_3 can balance the HDS activity and selectivity well.
- Co–Mo/Al_2O_3 prepared by macro-pore Al_2O_3 show weakening intra-particle diffusion.

GRAPHICAL ABSTRACT



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ABSTRACT

To improve the selectivity performance of CoMoS catalysts applied to the hydrodesulfurization (HDS) of fluid catalytic cracking (FCC) gasoline, a series of $CoMoS/Al_2O_3$ catalysts was prepared with alumina of different pore structures, and their HDS performance was evaluated with a real FCC gasoline. This study indicated that $CoMoS/Al_2O_3$ catalysts prepared with micro- or meso-porous alumina possessed high HDS activity but low HDS selectivity, whereas macro-porous alumina enhanced the selectivity of CoMoS catalysts. The enhanced HDS selectivity was due to the tuning of the MoS_2 slabs and the weakening of the internal diffusion resistance. Based on the above results, the optimal $CoMoS/Al_2O_3$ catalyst was prepared with the alumina of the tri-modal pore distribution at approximately 5–8 nm, 15–20 nm, and 90–100 nm. The optimal catalyst displayed a balanced HDS activity and selectivity in contrast to the reference catalyst prepared with K- and P-modified Al_2O_3.

1. Introduction

With the rapid growth in the number of civilian motor vehicles, an increasing amount of gasoline is consumed every year, and severe pollution is caused by tail gas. Therefore, governments have widely adopted new restrictive regulations for vehicle gasoline to

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reduce vehicle pollution, and some developed countries already claim to have restricted the sulfur content of gasoline to below 10 ppm. Fluid catalytic cracking (FCC) gasoline, produced by FCC units, makes up 30–50% of the commercial gasoline pools in the US and Europe, but this number can be as high as 80% in Asian countries [1]. FCC gasoline contributes approximately 90% of the total sulfur to the gasoline pool [2]. Hydrodesulfurization (HDS) is a process for removing sulfur from FCC gasoline, and it is widely applied in refineries. However, the conventional HDS process usually gives rise to olefin saturation, which results in a marked decrease in octane number [3–5]. Therefore, developing a highly selective HDS catalyst is a strong focus of research.

The HDS catalysts usually contain bi-metallic Co–Mo as the active component, and this is supported on alumina or other supports. The support plays an important role in the performance of HDS catalysts, including loading and dispersing the active component. Moreover, the diffusion and accessibility of the reactant are affected by the pore structures of the supports. Numerous efforts have been made to improve catalytic performance by altering the support, such as the application of ZrO, TiO_2, and MgO [6]. In addition, further studies on mixed oxides have been performed: e.g., TiO–Al_2O_3 [7,8] and TiO–SiO_2 [9]. Based on these mixed oxides, various correlations between the surface acid sites and the catalytic activity were proposed. In recent studies, the pore structures have attracted the attention of researchers. For example, the effects of the pore structure (based on SBA-15) on HDS performance have been studied [10,11], and it was concluded that both the pore size and the window size play an important role in the HDS activity. Considering ordered meso-porous alumina, Badoga et al. [12] systematically studied the effect of pore structure on improving the hydrotreating performance of Ni–Mo catalysts and reached the valuable conclusion that a high activity could be assigned to the high pore volume and surface area. The above two studies are valuable for the preparation of CoMo catalysts, but the pore diameter in these studies was limited to below 10.0 nm. Others prepared an egg-shell CoMoS/Al_2O_3 catalyst based on the idea that diffusion improved catalytic performance [13]. The results indicated that the egg-shell catalyst showed higher HDS activity and selectivity than did uniform catalysts due to its weakening of the internal diffusion resistance. Furthermore, modifications of alumina have been widely studied. For example, P and K elements have been added to improve catalytic performance, and the synergistic effect of both K and P was significant [14]. FCC gasoline is a fraction ranging from C_4 to C_{12}, and olefin molecules are easily trapped in the small pores of the catalyst during the HDS process [15], which can lead to an excess of hydrogenation and a severe decrease in octane number. The purpose of the present study is to improve the olefin adsorption, the number of active sites and the diffusion resistance.

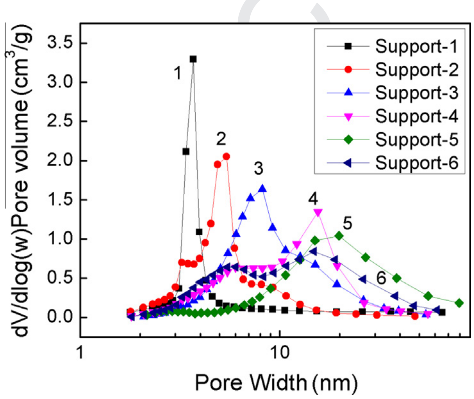

Fig. 1. Micro/meso-pore distributions of supports as determined by N_2 adsorption and desorption.

Table 1
Pore structures of supports as determined by N_2 adsorption and desorption.

Sample no.	S_{BET} (m^2/g)	PV (cm^3/g)	Average pore size (nm)	Centralized pore size (nm)
Support-1	219.1	0.41	5.7	3.5
Support-2	214.4	0.55	6.3	5.2
Support-3	184.4	0.42	10.7	10.2
Support-4	198.2	0.66	11.1	16.5
Support-5	187.6	0.69	18.5	20.0
Support-6	211.4	0.69	11.6	5.6/17.0

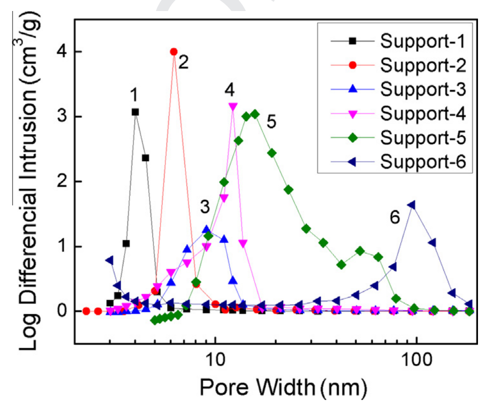

Fig. 2. Meso/macro-pore distributions of supports as determined by mercury porosimetry.

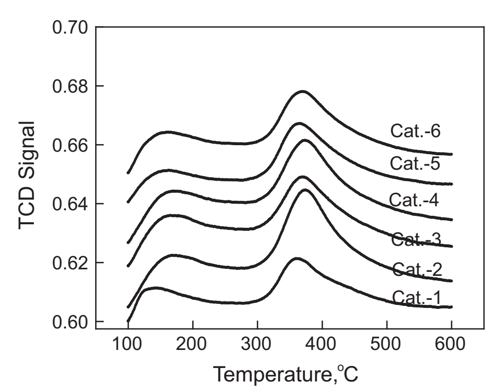

Fig. 3. TPD of the NH_3 curves of different catalysts.

Most of the methods in the literature are effective at improving the HDS performance. However, it is difficult to translate the process for oxides other than Al_2O_3. Alumina modification can increase the cost of catalyst preparation. There are some drawbacks in the preparation of egg-shell catalysts: e.g., the egg-shell thickness of the active components is difficult to control during the preparation process. Al_2O_3 is a traditional catalyst support and is still widely used in catalyst manufacturing because of its outstanding textural and mechanical properties, stability, and relatively low cost. Therefore, to tune the dispersion of MoS_2 slabs and to weaken the intra-particle diffusion resistance, we prepared a series of CoMoS/Al_2O_3 catalysts based on alumina with a pore width ranging from 3 to 100 nm, and the effects of the support pore structures on the dispersion of MoS_2 slabs and the