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# The Application of Mesoporous ZSM-5 Zeolite in the ULSD Catalysts

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## Abstract

The mesoporous ZSM-5 zeolite containing MoCoP/Al2O3 catalyst (C12-ZSM5) with the mixture of Al2O3 and mesoporous ZSM-5 zeolite as carrier was synthesized. The catalytic performance of C12-ZSM5 catalyst was evaluated by the hydrodesulfurization (HDS) of different diesel feedstock. The carriers and catalysts were characterized by N2 adsorption-desorption, pyridine-FTIR, X-ray diffraction (XRD) and CO in-situ FTIR (CO-FTIR) techniques. Results showed that mesoporous ZSM-5 can improve the acidity of the catalyst and increase the number of MoCoS active phases. The C12-ZSM5 catalyst had low HDS and HDN activity, because the acidic sites of mesoporous ZSM-5 were easily occupied by nitrogen compounds. The HDS activity of C12-ZSM5 catalyst was fully exploited by using graded packing technology, the sulfur content of product oil was 5.9 ng/μL. The relative HDS activity of C12-ZSM5 catalyst is 1.47 times that of FHUDS-8 catalyst.

**Keywords:** ZSM-5 zeolite; Hydrodesulfurization (HDS); Catalysts; Ultra-low sulfur diesel (ULSD)

## Introduction

The requirements that the diesel must meet in transport applications have been more stringent in the last decade. The sulfur concentration, a major impurity in crude oil, has been limited to no more than 10 ppm in many countries. There are several methods to product ultra-low sulfur diesel (ULSD), such as feedstock or crude oil selection, reducing the final point of feedstock, adding kerosene distillate, increasing operating temperature, utilizing the higher activity catalyst systems, building new hydrotreating units and so on. The most economical method is to use higher activity hydrodesulfurization (HDS) catalyst system [1].

The novel supports, active phases, promoters, or additives are used to improve the performance of the HDS catalyst. $MoS_2$ supported on alumina is promoted with Co or Ni [2]. An alternative material as carrier can greatly improve the HDS activity. A diversity of materials has been used as carriers, i.e., carbon [3], mixed oxides [4], and mesostructured silicas such as MCM-4 [5] and SBA-15 [6]. In our work, we apply mesoporous ZSM-5 in the ULSD catalysts.

## Experimental

Mesoporous ZSM-5 (Meso-ZSM-5) was synthesized from an aluminosilicate gel with mesoporous template. The mixture of ZSM-5, $\gamma$-$Al_2O_3$ and additives in a definite ratio was extracted, and then drying and calcination to produce supports. The carriers are referred as D*X*-ZSM5 (*X*= 25, 15, 12, 10, 8, 0) where *X* is the weight% of ZSM-5. The contrast support (D12-typical ZSM5) was prepared, and the typical ZSM-5 zeolite was synthesized according to the procedure reported in literature [7].

Mo-Co oxide precursors were prepared by impregnation of aqueous solutions of ammonium heptamolybdate and cobalt nitrate on the supports. The supports were treated in air at 100 °C for 6 h and then at 400°C for 3 h. The compositions were 18 wt.% $MoO_3$ and 3 wt.% CoO for the catalysts. FHUDS-8 catalyst was developed by Dalian Research Institute of Petroleum and Petrochemical, and the active metals were Mo and Ni.

The supports and catalysts were characterized by BET, SEM, IR, $H_2$-TPR and CO-FTIR. The HDS activity of the catalysts was evaluated using two types of straight-run diesel as raw oil. The sulfur and nitrogen concentrations of raw oil were 0.73 wt. %, 58.2 ppm and 1.42 wt. %, 389 ppm, respectively.

## Results and Discussion

Figure 1 showed the pore distribution of the Meso-ZSM-5 and typical ZSM-5. The most probable aperture of Meso-ZSM-5 was 2nm and 20nm. Compared with typical ZSM-5, the mesoporous structure of Meso-ZSM-5 was obvious. The 100nm small particles accumulated to form 5000nm large particles in the Meso-ZSM-5 (SEM result), and there were many intercrystalline pores between the small particles, which provided more space and active sites for the reaction comparing with typical ZSM-5.

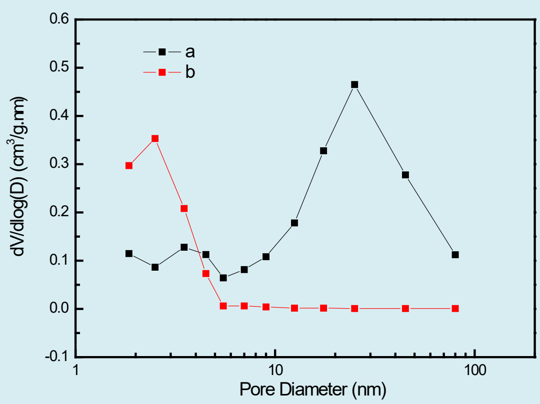


**Figure 1:** The pore distribution of meso-ZSM-5 (a) and typical ZSM-5(b).

The pore volume of D*X*-ZSM5 carriers decreased with the increase of Meso-ZSM-5, because the pore volume of Meso-ZSM-5 was smaller than that of $Al_2O_3$. The CO-FTIR results showed that the ratio of CoMoS active sites firstly increased and then decreased with the increase of Meso-ZSM-5. The CoMoS active sites of catalyst with 12% Meso-ZSM-5 content (C12-ZSM5) were the highest, which indicated the catalyst had best HDS activity.

The relative HDS activity of different catalysts was showed in Figure 2. The results indicated that the HDS activity of catalysts firstly increased and then decreased with the increase of Meso-ZSM-5, and the HDS activity of C12-ZSM5 was the best. Comparing with C0-ZSM5 ($Al_2O_3$ support), the relative HDS activity of C12-ZSM5 and C12-typical-ZSM5 was 126% and 94%, respectively, which indicated that the Meso-ZSM-5 could greatly improve the HDS activity.

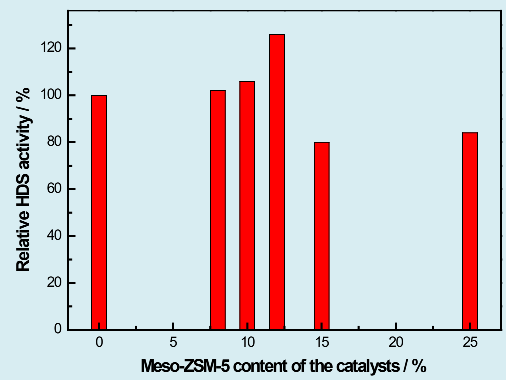


**Figure 2:** The relative HDS activity of catalysts.

The Meso-ZSM-5 could be poisoned by the nitrides of raw oil, so we adopted the FHUDS-8 (Mo-Ni) / C12-ZSM5 catalysts combination. The results showed that the sulfur content of product was 5.5 ppm for the FHUDS-8 (Mo-Ni) / C12-ZSM5 catalysts combination, while 10.7 ppm for FHUDS-8 catalyst at the same operation conditions. The relative HDS activity of FHUDS-8 (Mo-Ni) / C12-ZSM5 catalysts combination was 1.47 times higher than that of FHUDS-8 catalyst.

## Conclusions

The HDS activity of catalysts firstly increased and then decreased with the increase of Meso-ZSM-5, and the HDS activity of the catalyst with 12% Meso-ZSM-5 (C12-ZSM5) was the best. The relative HDS activity of FHUDS-8 (Mo-Ni) / C12-ZSM5 catalysts combination was 1.47 times higher than that of FHUDS-8 catalyst.

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