Chapter 15
Preparation, Characterization and Desulfurization of the Supported Nickel Phosphide Catalysts

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ABSTRACT

Hydrodesulfurization (HDS) is an important technology to produce clean fuels, in which the nickel phosphide catalysts exhibit excellent catalytic performances. In this work, a series of Ni_xP/SBA-15 catalysts with various P/Ni molar ratios were prepared using the mesoporous molecular sieve SBA-15 as the support. The structure and surface properties of the catalysts were characterized by X-ray diffraction (XRD), N_2 sorption analysis, transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FTIR), and in situ diffuse reflectance infrared Fourier transfer spectroscopy (DRIFTS). The catalytic performances for the HDS of dibenzothiophene (DBT) were evaluated. The results demonstrated that the Ni_xP/SBA-15 catalysts possessed high specific surface area and the mesoporous structures, which benefited the elimination of the internal diffusion limitation in the HDS reactions. Both Ni_2P and $Ni_{12}P_5$ phases showed catalytic activity in HDS reactions while Ni_2P was more active. The optimal P/Ni molar ratio was about 0.75. The DBT conversion can reach 95.8% under the reaction condition of pressure at 3.0 MPa, H_2:oil=600, WHSV at 26.7 h^{-1}, and temperature at 340ºC. In situ DRIFTS spectra indicated that the coordinative unsaturated $Ni^{\delta+}$ (0<δ<1) species on the catalysts surface were the active sites for the HDS of DBT.

INTRODUCTION

The exhaust emission, especially the SO_2 emission, has attracted more and more attentions by the governments all over the world due to the developments of automobile industry and increasingly grievous situation in environmental protections. Accordingly, more and more stringent environmental regulations have been enacted to limit the S content in the fuels. To meet the regulations, most of the S should be eliminated by the deep hydrodesulfurization (HDS) during the petroleum refining processes. It is difficult to remove the S content to ultra-low levels using a conventional $Mo(W)Co(Ni)/Al_2O_3$ HDS catalyst. The transition metal phosphides are reported as a novel catalytic material with exceptional HDS performances, showing great prospect as the new generation of catalysts in deep HDS. Among the transition metal phosphides, nickel phosphide showed the best activity. Previously the nickel phosphides were usually supported on Al_2O_3 or SiO_2. The specific surface areas of Al_2O_3 or SiO_2 supported catalysts were relatively low, which was unfavorable for the dispersion of the active phases, leading to an unsatisfactory activity or stability. The mesoporous molecular sieve SBA-15 was regarded as a superior support due to the higher specific surface area, higher pore volume and narrower pore size distribution.

In the present work the mesoporous molecular sieve SBA-15 was synthesized via hydrothermal method using the cheap sodium silicate as the silicon source, the triblock copolymer (P123, $EO_{20}PO_{70}EO_{20}$) and cetyltrimethyl ammonium bromide (CTAB) as the co-template reagents. The $Ni_xP/SBA-15$ catalysts with a fixed Ni content of 20 wt% and a varying initial P/Ni molar ratio (0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0) were prepared by a co-impregnation method using $Ni(NO_3)_2 \cdot 6H_2O$ as the nickel source, $(NH_4)_2HPO_4$ as the phosphorus source and SBA-15 as the support, and following by the H_2 temperature-programmed reduction (H_2-TPR) treatment.

The phase formation, specific surface area and pore structure of the prepared catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 sorption analysis and Fourier transform infrared spectrometry (FTIR) techniques. The nature of the active sites on the surface of the catalysts was investigated by CO adsorption using *in situ* diffuse reflectance infrared Fourier transfer spectroscopy (DRIFTS). The HDS of dibenzothiophene (DBT) was employed as a model reaction to test the HDS performances of the catalyst. The effects of the external diffusion, the internal diffusion, the total pressure, the volume ratio of H_2 to liquid feed, and the reaction temperature on the activity of the catalyst was examined systematically. The stability of the catalyst and the evolution of the structure during the stability test were investigated as well.

The obtained results showed that with the cheap sodium silicate as the silicon source, the prepared mesoporous molecular sieve SBA-15 had the specific surface area (S_{BET}) of 674.0 m^2/g, the pore volume (V_P) of 1.12 m^3/g and average pore diameter (D_{BJH}) of 6.7 nm. For the prepared $Ni_xP/SBA-15$, Ni_2P and $Ni_{12}P_5$ phases existed at P/Ni = 0.5. Only Ni_2P phase was detected at P/Ni ≥ 0.75. Both Ni_2P and $Ni_{12}P_5$ phases showed catalytic activity in HDS reactions while Ni_2P was more active. The optimal P/Ni molar ratio was found at 0.75. Either too high or too low P/Ni molar ratio would lead to a diminished HDS activity. The mesoporous structure was mainly maintained with the P/Ni molar ratio ranging from 0.25 to 2.0. All of the $Ni_xP/SBA-15$ catalysts had high S_{BET} and V_P as well as uniform pore size distribution, which would benefit the dispersion of the active phases on the catalysts and the diffusion of reactants during HDS reactions.

The prepared $Ni_xP/SBA-15$ catalysts exhibited good activity in the HDS of DBT, among which the $Ni_xP/SBA-15$ (P/Ni=0.75) catalyst possessed the highest DBT conversion. The DBT conversion of the $Ni_xP/SBA-15$ (P/Ni=0.75) catalyst reached 95.8% at 340 ºC, under 3.0 MPa, with the volume ratio of

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