Promotional Effect of Ga for Ni_2P Catalyst on direct hydrodesulfurization of 4,6-DMDBT

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Abstract: The $Ni_2P/Ga(x)-SiO_2$ catalysts were prepared with varying the content of Ga and applied for the hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiphene (4,6-DMDBT). The structural and chemical properties of the catalysts were characterized by XRD, BET, EXAFS, FT-IR, TEM, and CO uptake measurements. The HDS activity was tested at 3.0 MPa and 613K in a three-phase fixed-bed reactor using a model feed containing 500 ppm S as 4,6-DMDBT, 6000 ppm S as DMDS, 200 ppm N as quinoline, 1 wt% tetralin, and 0.5 wt% n-nonane in n-tridecane balance. It was demonstrated that the DDS selectivity is enhanced if 1.0 wt% Ga was loaded on the Ni_2P catalyst.
Keywords: hydrodesulfurization, Ni_2P, gallium, 4,6-dimethyldibenzothiophene

1. Introduction

With stricter environmental regulation on the emissions of pollutants, the role of desulfurization process in the refining industry has become more important in the past decades [1]. In order to treat refractory S compounds conventional NiMoS catalysts require severe conditions especially of a high H_2 consumption. As alternatives to the conventional catalysts Ni_2P has recently been introduced and shown a high and stable activity [2]. For example, it has been reported that Ni_2P shows two-fold HDS activity relative to $Co-MoS_2$ catalyst in the HDS of dibenzothiophene [1]. The HDS follows two reaction pathways of direct desulfurization (DDS) and prehydrogenation (HYD) followed by hydrodesulfurization. For a sterically hindered S compound, i.e. 4,6-DMDBT it is known to follow HYD pathway over the conventional catalysts, consuming more H_2. It is thus required to develop a new catalyst which is more active in DDS pathway. This study focuses on the effect of Ga addition on the Ni_2P catalysts to investigate the HDS selectivity of 4,6-DMDBT.

2. Experimental

The $Ni_2P/Ga(x)-SiO_2$ catalysts were prepared with 0, 0.5, 1.0, and 2.0 wt.% of gallium loadings. The $Ga(x)-SiO_2$ were synthesized by incipient wetness impregnation of aqueous solutions of gallium nitrate. After impregnation, the supports were dried at at 353 K for 12 h and calcinated at 723 K for 4 h. The amount of Ni loading was fixed at 1.0mmol Ni/g support. Thereafter, the catalyst synthesis was carried out by the same method in the previous study [3]. The catalytic HDS activity was tested at 3.0 MPa and 613K in a three-phase fixed-bed reactor using a model feed containing 500 ppm S as 4,6-DMDBT, 6000 ppm S as DMDS, 200 ppm N as quinoline, 1 wt% tetralin, and 0.5 wt% n-nonane in n-tridecane balance. The liquid was delivered at 2ml per hour with 50 ml per minute of H_2 flow [4]. The catalyst samples were analyzed by X-ray diffraction(XRD), N_2-adsorption specific surface area measurements, extended X-ray absorption fine structure measurements (EXAFS), Fourier transform infrared (FT-IR), transmission electron microscopy (TEM) analysis, and CO uptake measurements.

3. Results and discussion

Fig. 1 compares the HDS activity, and selectivity toward HYD and DDS pathways over the catalysts. Overall, the $Ni_2P/Ga(x)-SiO_2$ catalysts exhibit a high HDS conversion over 96%. However, the HDS selectivity was found to differ, particularly for $Ni_2P/Ga(1.0)-SiO_2$. which exhibits the DDS selectivity over 33%. Fig. 2 shows the FTIR spectra of CO chemisorbed $Ni_2P/Ga(x)-SiO_2$. The Ga-free Ni_2P catalyst exhibited $\nu_{C=O}$ band at 2064 cm^{-1}. However, the addition of Ga on the catalysts shifted the band to a higher frequency, indicating a stronger C-O bonding. This can be explained by an electron deficient nature of Ni_2P surrounded by GaOx species.

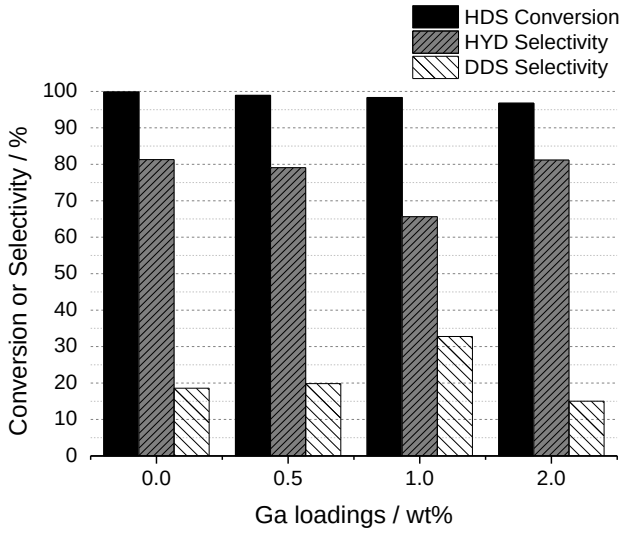

Fig.1 HDS conversion, HYD and DDS selectivity depending on the loading amount of Ga (LHSV=2h^{-1}, 50ccm H_2 flow)

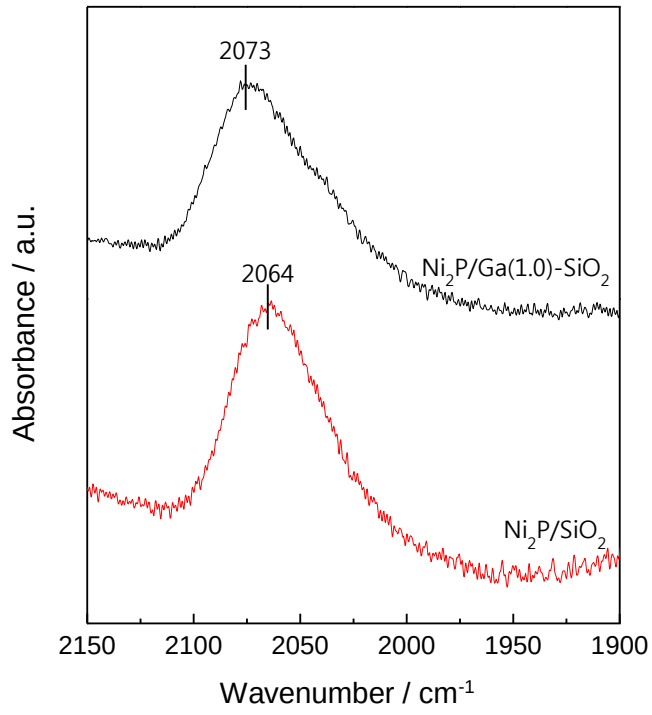

Fig.2 FTIR spectra of CO adsorption over Ni_2P/(Ga)-SiO_2 catalysts

4. Conclusions

The effect of Ga addition on the Ni_2P catalyst for the HDS of 4,6-DMDBT was investigated. A proper loading of 1.0 wt% Ga on Ni_2P/Ga(x)-SiO_2 leads to a rise of DDS selectivity, which was likely due to the enhanced S adsorption capability of electron-deficient of Ni_2P catalyst particularly in the presence of GaOx.

References

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