

Nickel-citrate complex effect for supported NiWS hydrodesulfurization catalysts

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Introduction

The main challenge in deep hydrodesulfurization (HDS) of gas oil fuels consists in improving the catalytic activity towards the refractory alkyl-dibenzothiophene (alkyl-DBT) molecules. In this sense, the mixed “Ni-W-S” phase possesses an outstanding hydrogenation of aromatic rings (HYD) capacity, and it has shown high potential for HDS [1]. However, the complete formation of the active mixed phase is hardly achieved due to the premature Ni sulfidation within W, leading to segregation of NiS_x and WS₂. Additionally, the Strong Metal-Support Interaction (SMSI) induces incomplete W sulfidation and a decrease in the availability of Ni to promote the WS₂-edges fraction [2]. The use of modified Al₂O₃ supports, such as the equimolar Al₂O₃-TiO₂ oxide successfully decreased SMSI and preserved suitable textural properties. These improvements increased the metallic availability on the surface, but WS₂-edge promotion was not significantly improved [3]. Recently, the use of the aqueous [Ni(Cit)₂(H₂O)₄]⁴⁺ (NiCit₂) complex during NiW/Al₂O₃ catalysts synthesis led to a more abundant and better dispersed “Ni-W-S” phase than [Ni(H₂O)₆]²⁺ species, and with significant increases in catalytic activity for HDS reaction [4]. Therefore, the aim of this work was to investigate the effect of aqueous (NiCit₂) complex as Ni precursor on the HDS catalytic activity of supported WS₂-edges in NiWS supported on Al₂O₃ and Ti-modified Al₂O₃.

Materials and Methods

(Nickel-Citrate)-Tungsten (CNiW) and nickel-tungsten (NiW) catalysts (2.8 W-nm⁻² and atomic Ni/(W+Ni)= 0.4) supported on Al₂O₃, and on Al₂O₃-TiO₂ mixed oxide (named as AT2, molar ratio Al/Ti= 2) were prepared by subsequent incipient wetness impregnation method. ICP-AES determined the real metal loadings. Details catalysts syntheses are found in previous work [3,4]. The pH of the nickel-citrate solution was optimized to obtain the maximum concentration of the Ni-Cit₂ complex. For this, thermodynamic calculations and spectroscopic characterization were performed. Catalysts characterization was carried on oxide- and sulfide-state by DRS UV-Vis, TPR, XPS and HRTEM techniques. The catalysts were sulfided ex-situ with a gas mixture (10 %)H₂S/H₂ at 673 K for 2 h. Sulfided catalysts were evaluated in 4,6-dimethyldibenzothiophene (46DMDBT) HDS reaction (300 ppm of S, 593 K, and 5.4 MPa in a reactor operating in batch mode). Products quantification was carried out by gas chromatography. Catalytic activity was expressed as turnover frequency (TOF=reaction rate/W-edges atoms as WS₂; molec·(site·h)⁻¹). W-edges atoms in a WS₂ slab were calculated from XPS and HRTEM measurements.

Results and Discussion

From equilibria calculations, the maximum molar fraction (~0.92) of NiCit₂ complex was reached at pH 5 in nickel-citrate solution, while [Ni(H₂O)₆]²⁺ was the unique Ni complex in the impregnation solution without citric acid. UV-Vis and FTIR-ATR spectroscopy confirmed these findings. DR UV-Vis spectroscopy analyses suggested the formation of Ni(Cit₂) surface complexes during the dry/ripen step. This surface complex was related to an important increase in the nickel reduction temperature (340→430°C), which led to the simultaneous reduction of higher fractions of Ni and W species as compared with the catalysts prepared with [Ni(H₂O)₆]²⁺ complex. Moreover, the re-dispersion of WO_x species due to Ni(Cit₂) incorporation was evidenced. For sulfided catalysts, a significant increase in W sulfidation (WS₂) and WS₂-edge promotion (NiWS; Figure 1) was pointed out when Ni(Cit₂) compound was used as Ni precursor, as well, smaller WS₂ particles were observed by HRTEM. If the Ni-isolation effect provided by Ni(Cit₂) is extrapolated to sulfidation step, simultaneous metal sulfidation may explain the increase in the mixed “NiWS” phase fraction. The TOF values for CNiW catalysts were 3-5 times higher than those obtained when [Ni(H₂O)₆]²⁺ was used (NiW; Figure 2). The incorporation of the NiCit₂ complex modified the metal-support interactions favorably, resulting in significant increases in specific catalytic activity for 46DMDBT hydrodesulfurization.

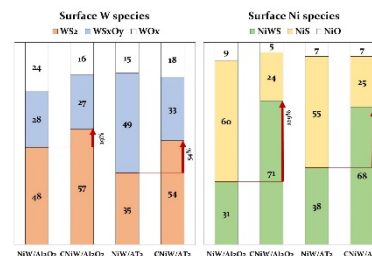


Figure 1. Superficial composition of W and Ni entities of sulfided catalysts

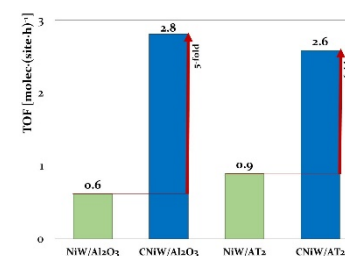


Figure 2. TOF [molec·(sites·h)⁻¹] for NiW and CNiW catalysts supported

Significance

This work evidenced a remarkable increase in specific catalytic activity (molec·(site·h)⁻¹) for the HDS of refractory alkyl-dibenzothiophenes of supported NiWS catalysts, by the influence of the key [Ni(Cit₂)(H₂O)₄]⁴⁺ complex.

References

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