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Heavy oil hydrodenitrogenation on titanium-modified Al2O3-supported NiWS catalysts: Effects of modification method

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Hydrotreating (HDT) is considered to be the most direct and effective techniques to realize the efficient conversion of inferior heavy oil into light products and high value-added chemical raw materials. And hydrodenitrogenation (HDN) is regarded as the most difficult and representative reaction in the heavy oil HDT process. In order to further improve the HDN performance of the existing HDT catalysts and explore the structure-activity relationship of the catalysts, γ-Al2O3 supports were modified with a Ti/Al molar ratio of 1 by three different methods: the mechanical mixing method, the ion-exchange method and the in-situ synthesis method, and the corresponding NiW supported HDT catalysts were prepared via incipient wetness co-impregnation method. The effects of Ti modification on the physicochemical properties of the prepared supports and catalysts were determined by the characterization techniques such as XRD, FTIR, N2 physical adsorption-desorption, SEM, Py-FTIR, H2-TPR, HRTEM and XPS. Finally, quinoline, indole and coker gas oil (CGO) were used respectively as probes to investigate the Ti modification on the HDN performances of the corresponding catalysts. The results show that the introduction of TiO2 into γ-Al2O3 would changes the pore properties and reduces the acid strength of the supports, weakens the interaction between the active metals and the supports (MSI), and can promote the formation of more so-called "type II" NiWS active phases and enhance the sulfidation degrees of active metals. According to the study on different Ti modification methods, we found that the *in-situ* synthesis method realizes the molecular composition of titanium and aluminum elements, showing the most favorable composite effect, followed by the ion-exchange method, and the mechanical mixing method was found to exhibit the worst composite effect. And Ti3+ species were found in the sulfided catalysts prepared by in-situ synthesis method and ion-exchange method. This leads to the fact that in terms of the promotion of active metal dispersion and sulfidation degrees, the in-situ synthesis method is always the best, followed by the ion exchange method and finally the mechanical mixing method. The catalytic assessment results show that the HDN activities of the catalysts were effectively improved after Ti modification and the HDN activities are consistent with the composite effect of titanium and aluminum elements and the dispersion and sulfide degrees of active metals. Among the three investigated modification methods, the in-situ synthesis method was found to be the most favorable for preparing high HDN activity catalysts for heavy oil.

Conclusion: In this study, we employed three different methods, the mechanical mixing method, the ion-exchange method and the in-situ synthesis method to synthesize Ti modified γ-Al2O3 supports with a Ti/Al molar ratio of 1, and prepared the corresponding NiW supported HDT catalysts via incipient wetness co-impregnation method. The effects of Ti modification method on the physicochemical properties of the supports and the catalysts and the catalytic performances of the corresponding catalysts were investigated. The

main conclusions can be summarized as follows: (1) the Ti modification method affects the textural properties and the acidity of the supports, the MSI, and the morphology of the NiWS active phase of the corresponding catalysts; (2) Compared with the other two methods, the in-situ synthesis method exhibits the best titanium-aluminum composite effect, achieving the level of molecular composition; (3) In terms of the promotion of active metal dispersion and sulfidation degrees, the in-situ synthesis method is always the best, followed by the ion exchange method and finally the mechanical mixing method; (4) The HDN activities of the catalysts were effectively improved after Ti modification and the HDN activities are consistent with the composite effect of titanium and aluminum elements and the dispersion and sulfide degrees of active metals. The in-situ synthesis method is the most favorable modification method for preparing high HDN activity catalysts for heavy oil.

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Biography

Wenbin Huang PhD, student in chemical engineering and technology in china university of petroleum, was born in Jiangxi china. Bachelor of engineering, chemical engineering and technology-2018 china university of petroleum, Beijing, china. Then, he begin to study for a doctorate in engineering in china university of petroleum, Beijing, majoring in petroleum and natural gas chemistry. Over the past postgraduate career more then 10 articles have been published in international renowned journals.

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