Unsupported layered bimetallic sulfide catalysts and their hydrodenitrogenation performance

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Abstract: Unsupported layered multi-metallic sulfide catalysts exhibit superior hydrodesulfurization performance because of their ultra-high hydrogenation activities, but it is not known if they are also active in hydrodenitrogenation. Herein, a series of layered bimetallic and trimetallic sulfide catalysts were prepared, characterized and evaluated for hydrodenitrogenation reactions using quinoline and decahydroquinoline as N-containing model compounds. It is found that WS2 in such catalysts has higher HDN activities than MoS2, and the catalysts with the Mo/Ni or W/Ni atomic ratio of 0.3 show the highest HDN performance among those bimetallic sulfide catalysts NiMoSx and NiWSx.

Keywords: unsupported bimetallic sulfide catalyst, layered structure, hydrodenitrogenation.

1. Introduction

Hydrodenitrogenation (HDN) is crucial for hydrocracking and hydrodesulfurization (HDS) because of the poisoning effect of basic N-containing compounds on active sites of the catalysts. Due to the hydrogenation steps are indispensable to HDN reactions, the hydrotreating catalysts with higher hydrogenation activities usually exhibit better HDN performance. In our previous work, unsupported layered multi-metallic sulfide catalysts was prepared and showed high activities in hydrogenation reactions. Therefore, they presented much higher HDS activities than commercial CoNiMoWSx/Al2O3 catalysts in the HDS process of 4,6-DMDBT. However, it is not known whether they are also active in the HDN process. Also, the influences of the compositions of the catalysts on their texture properties and catalytic performance remains unclear. Hence, in this work, unsupported layered bimetallic sulfide catalysts NiMoSx and NiWSx are prepared, characterized and evaluated for the HDN performance of N-containing model compounds, and the contribution of individual components, MoS2 and WS2, is clarified.

2. Experimental

Unsupported layered bimetallic sulfide catalysts NiMoSx and NiWSx with different metallic molar ratio were prepared by ion exchange reactions using Ni-LHS precursors. The corresponding catalysts NiMoSx and NiWSx were denoted as NiMo-x and NiW-x based on their Mo/Ni or W/Ni atomic ratio, respectively. The catalysts were evaluated on a high-pressure fixed-bed continuous flow microreactor using a model diesel with 500 ppm of N, while quinoline and decahydroquinoline (DHQ) were adopted as N-containing compounds. The reaction was carried out at 310 °C, 3.5 MPa, H2/oil ratio of 600 Ncm3/cm3 and LHSV of 9.0 h⁻¹. According to the HDN product distribution, the HDN activity (N removal%) could be calculated as follows:

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N \text{ removal} \% = \frac{\sum C_{HC,i} - \sum C_{N,i}}{\sum C_{HC,i} + \sum C_{N,i}} \times 100\%
\]

Where the \( C_{HC,i} \) represent the mass fractions of each hydrocarbon products in all products and reactant, and the \( C_{N,i} \) represent the mass fractions of each N-containing products and the reactant in all products and reactant.

3. Results and discussion
As shown in Figure 1, the NiS<sub>x</sub> only exhibited a trace of HDN activity for the HDN of quinoline, but over 10% of N removal for the HDN of decahydroquinoline. In contrast, the HDN activities of each unsupported bimetallic sulfide catalysts NiMoS<sub>x</sub> and NiWS<sub>x</sub> were scarcely influenced by the alternate of those two N-containing compounds as reactant. Moreover, the HDN activity increased with the increasing Mo or W content while the Mo/Ni or W/Ni atomic ratio was lower than 0.3, and then began reducing with the increase of Mo or W content. Furthermore, the HDN activities of NiWS<sub>x</sub> were evidently higher than NiMoS<sub>x</sub> under the same metallic molar ratio, indicating that WS<sub>2</sub> was higher active than MoS<sub>2</sub> in such catalyst for HDN.

![Figure 1. Catalytic activities of unsupported bimetallic sulfide catalysts for HDN of different N-containing compounds: (black) quinoline over NiMoS<sub>x</sub>; (red) DHQ over NiMoS<sub>x</sub>; (blue) quinoline over NiWS<sub>x</sub>; (green) DHQ over NiMoS<sub>x</sub>. Reaction conditions: 310 °C, 3.5 MPa, H<sub>2</sub>/oil ratio of 600 Ncm<sup>3</sup>/cm<sup>3</sup>, LHSV of 9 h<sup>-1</sup>.](image)

4. Conclusions

The HDN activities of unsupported layered multi-metallic sulfide catalysts were affected by their active metal contents, and the catalysts with the metallic molar ratio of 0.3 exhibited the best HDN performance. Besides, WS<sub>2</sub> showed higher activity than MoS<sub>2</sub> in such catalyst for HDN, so it would be the better choice for the catalysts used in the industrial HDN processes.

References