Selective Hydrotreating of Heavy Oil over Multifunctional Catalysts for BTX Production

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1. Introduction

Recently, the increasing global demand for energy and chemicals has driven more efficient petroleum conversion processes. Ethylene cracker bottom oil (ECB), a byproduct of petroleum processing, typically contains sulphur compounds and polycyclic aromatic hydrocarbons (PAHs) that are difficult to upgrade[1)]. Hydrogenation, ring opening, and dealkylation processes could convert PAHs into benzene, toluene, and xylene (BTX). As key raw materials in the chemical industry, producing BTX from low-value fractions is highly important. However, developing optimal catalysts remains challenging, making the design of multifunctional catalysts with balanced metal–acid properties essential. Therefore, in this study a series of NiW/ZSM-5 catalysts were developed and evaluated for BTX production from real feedstock. The effect of active metal loading, chelating agent addition and acid metal balance on catalytic performance were investigated.

2. Experiment

The support was prepared by mixing commercial ZSM-5 powder with an alumina binder named AP-1. The mixture was shaped into cylindrical extrudates, dried at 120°C and calcined at 600°C. Tungsten (W) was introduced via impregnation with or without citric acid (CA) addition during the impregnation and dried at 120°C. Nickel (Ni) was also loaded by impregnation according to the same procedure. NiW/ZSM-5–Al catalysts prepared contained 2.6, 3.2, 4 wt% of NiO and 16, 20, 25 wt% of WO_3. All catalysts were characterized by means of BET measurement, XRD, H_2-TPR and XPS. Catalytic activity was evaluated in a fixed bed flow reactor using a real oil-PAN Oil. Reactions were conducted under the condition 7 MPa of hydrogen pressure, LHSV of 2 h^{-1}, an H_2-to-feedstock volume ratio of 2000 and a temperature range of 340°C-400°C. Catalysts were pretreated via in-situ pre-sulfidation. The identification and quantification of liquid product was performed by GC-FID and GC-MS, and the gas product was performed by GC-FID.

3. Results and Discussion

The hydrotreating of PAN Oil leads to formation of light gases (C_1 to C_6), valuable aromatics such as BTX and other products through hydrogenation, hydrocracking, and aromatization reactions. Fig. 1 shows the product distribution in hydrotreating of PAN Oil over various catalysts. Increasing temperature from 340°C to 400°C promoted the conversion of polycyclic aromatic hydrocarbons (PAHs) to BTX formation, which is corresponding by a decrease in the heavy aromatic fraction.

The BTX formation increases progressively with an increase in the WO_3 loading, starting from 2.6Ni16W(CA)/Z5-Al to 3.2Ni20W(CA)/Z5-Al and reaching a maximum over 4Ni25W(CA)/Z5-Al. On the other hand, tetralin decreases gradually at elevated temperature, whereas naphthalene shows relatively minor variation compared to BTX and tetralin. The result demonstrates that increasing temperature and WO_3 loading leads the product distribution toward higher BTX formation. XRD analysis confirms that the ZSM-5 framework is preserved after metal incorporation, suggesting that the metal species are well dispersed, which may contribute to the observed catalyst performance.

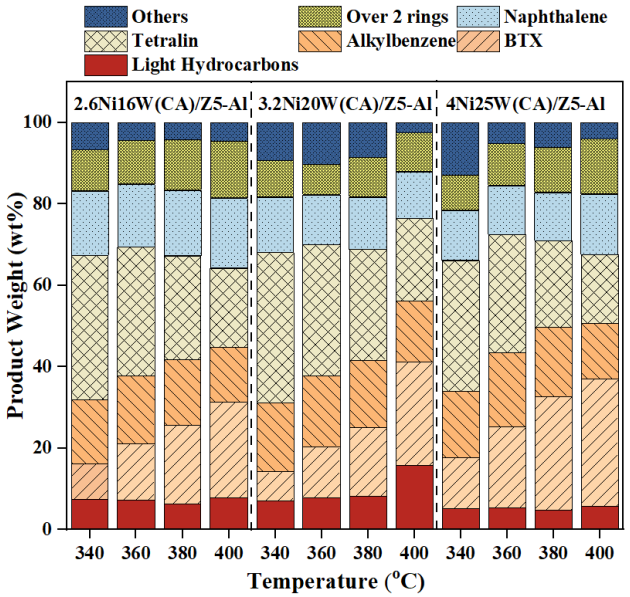

Fig. 1 Product distribution in PAN Oil hydrotreating over various catalysts

1) Zuo, Q., 55th Petroleum-Petrochemical Symposium of the JPI, Koriyama, 2025.

