Catalytic hydrotreatment using NiMo/MAS catalysts synthesized from ZSM-5 nano-clusters

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ABSTRACT

Mesostructured alumino-silcate (MAS) materials were synthesized from ZSM-5 nano-clusters and used as catalysts supports for the hydrotreatment of a model compound and real feed stock. Supports and catalysts were thoroughly characterized by using XRD, N_2 adsorption analysis, FT-IR, ^{27}Al MAS NMR, Raman, EXAFS and HRTEM techniques. The alumino-silicate materials exhibited different acid strength and textural properties depending on the duration of hydrothermal treatment of the zeolite seeds. Materials synthesized with low seeding time of 4 h showed properties similar to Al-SBA-15 prepared using the direct synthesis route, whereas material with high seeding time (t_{seed} = 24 h) resembled ZSM-5. The EXAFS study of the sulfided catalysts revealed that sulfidation was highest in the NiMo catalyst supported on mesoporous alumino-silicate synthesized from ZSM-5 seeds with 16 h of hydrothermal treatment (MAS-16). Hydrotreating experiments were conducted using model compound (DBT) at 325 °C and 600 psi as well as real feed stock (Coker light gas oil) at industrial conditions. Catalytic activity in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) was found to be maximum for this particular catalyst (MAS-16). The same catalyst also gave higher hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) conversion than NiMo/γ Al_2O_3 in the hydrotreating of Light Gas Oil.

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1. Introduction

Catalytic hydrotreating for the reduction of sulfur content in gasoline and diesel fuels has been an area of intensive research recently. Stringent environment legislations have meant that sulfur content in gasoline and diesel fuel be lowered to 10–50 ppm in most countries [1,2]. Consequently, hydrodesulfurization (HDS) catalysts with improved activity, product selectivity and longevity are needed to meet the stricter sulfur specifications of transportation fuels. Past studies have shown that the removal of refractory molecules like DBT and 4,6 DMDBT poses the greatest challenge for achieving ultra-low levels of sulfur [3]. One of the most promising approaches towards improving the performances of hydrotreating catalyst is the replacement of the conventionally used alumina by zeolites and other related acidic materials as supports for the CoMo and NiMo sulfide phases. These acidic materials have high surface areas for metal dispersion and a higher concentration of Bronsted and Lewis acid sites compared to alumina. A synergetic effect arising from the presence of both hydrogenating and strong acid sites not only accelerates the direct cleavage of the C—S bond but also promotes alternate pathways to the removal of sulfur atom from the aromatic molecule. This effect is especially pronounced in the HDS of 4,6 DMDBT, where isomerization of 4,6 DMDBT to 3,6 DMDBT improves the rate of C—S bond scission [4,5]. Regardless of their favorable acidic properties, zeolites are essentially microporous systems (pore size <2 nm) which severely limits their applications in the field of hydrotreating bulky molecules [6,7]. As a result, there is a continuous interest in synthesizing materials that not only possesses the high surface area and strong Bronsted acid sites of zeolites but also have a more open porous system preferably with a narrow pore size distribution in the mesoporous range.

Mesoporous silica materials such as MCM-41, HMS, SBA-15 and KIT-6 with open porous channels are ideal catalyst supports for the catalytic conversions of large molecules as they can overcome the diffusion barrier for reactants and products [3,8–10]. In spite of their excellent textural properties the applications of these materials in catalytic reactions where acidity plays an important role is very limited. This restriction stems from the absence of strong Bronsted acid sites as their surface is predominantly made of silanol groups [11]. In order to overcome the disadvantages of both zeolites and siliceous mesoporous materials, various teams have synthesized materials with strong acidity in open porosity through the surfactant based assembly of zeolite nano-clusters present in the precursors that nucleate to form the final crystalline zeolite. This

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