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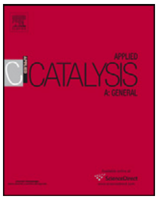

Application of different pore diameter SBA-15 supports for heavy gas oil hydrotreatment using FeW catalyst

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ABSTRACT

This work focuses on utilizing mesoporous SBA-15 materials of different pore diameters as potential hydrotreating catalyst supports for heavy gas oil (HGO). Hexane was used as swelling agent for the preparation of variable pore diameter SBA-15 materials. Four kinds of SBA-15 supported FeW catalysts with different pore diameters in the range of 5–20 nm were prepared and designated as Cats-A to D. The aqueous co-impregnation technique was employed for preparation of the catalysts. The supports were characterized by several techniques including X-ray powder diffraction (XRD) and N_2 adsorption–desorption isotherms. The SBA-15 supported FeW catalysts were characterized by ICP-MS, BET surface area analysis, powder XRD, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and CO chemisorption. Results from XRD profiles, TEM images, and N_2 adsorption–desorption isotherms confirmed the presence of highly ordered two-dimensional hexagonal structure with cylindrical arrays of pores. The structural integrity of the samples was preserved even after loading of 2 wt.% Fe and 15 wt.% W. Hydrotreating experiments were conducted using bitumen derived heavy gas oil under industrial conditions of temperature, pressure, LHSV, and gas to oil ratio of 375–400 °C, 8.8 MPa, 1 h^{-1}, and 600 mL/mL, respectively. The SBA-15 supported catalyst with pore diameter of 10 nm (Cat-B) was the best among the supports studied for FeW catalysts, probably due to sufficient mass transfer of reactant liquids and gases through the catalyst's pores while still maintaining a high surface area necessary for metal dispersion.

1. Introduction

The hydrotreatment of petroleum feedstocks mainly aims to produce clean gasoline and diesel with low sulfur, nitrogen and aromatic contents. More stringent environmental regulations have required improved efficiency of these processes [1]. Industrially, the most commonly used hydrotreating catalyst is the γ-Al_2O_3 supported molybdenum sulfide, MoS_2, (10–20 wt.%), which is typically promoted with cobalt or nickel (3–5 wt.%). However, the traditional γ-Al_2O_3 support has a fairly broad pore size distribution with a considerable portion of the total surface area in small pores, specifically, pores less than 5 nm in size [2]. The pore diameter of the catalyst support plays a crucial role in its overall catalytic performance by enhancing diffusion of reactant molecules to catalytic active sites predominantly located inside the pores [1]. As in the case of γ-Al_2O_3 support, active metals in such pores may not be readily accessible to bulkier molecules (such as the alkyl-substituted dibenzothiophenic compounds) and may also suffer severe sintering in the pores as a result of exposure of these dispersed nanocrystalline materials to high hydrotreating temperatures.

The issue of rapid initial catalyst deactivation is of prime concern with commercial γ-Al_2O_3 supports due to pore plugging of smaller pores (<5 nm) [2]. Moreover, diffusional limitation associated with γ-Al_2O_3 during operation with heavy petroleum fractions presents a major drawback to the full utility of such supports in hydroprocessing heavier feedstocks. However, for an enhanced hydrotreating activity, the pore size distribution of the support should be narrow and the pore diameter must be large enough to overcome most diffusional restrictions. Furthermore, too large a pore diameter also leads to further decrease in surface area, which might result in decreased HDT activity [3]. Supports that offer large pore diameter while maintaining desirably high surface area for great dispersion of supported metals will help minimize the major diffusional problem of γ-Al_2O_3 support.

The development of HDT catalysts has significantly progressed over the years; however, major focus has been to identify support materials of improved and attractive textural properties [4]. In the quest to enhance catalytic activities via the option of changing HDT catalyst supports, many carriers other than gamma alumina

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have been investigated. These include clays [5], carbon [6], oxides [7,8], mixed oxides [9,10], zeolites [11] and mesoporous materials like MCM-41 [12], HMS [13], SBA-15 [14], and KIT-6 [15,16].

Ordered mesoporous solids such as HMS, MCM-41 and MCM-48 [17] have great potential as hydrotreating catalyst supports. They have several advantages over conventional catalyst supports, e.g., high surface (area around 1000 m^2/g) that can provide better distribution of active metal components and more adsorption sites, and a large tunable mesopore size (ranging from 5 to 30 nm). Their large mesoporous channels can overcome the steric hindrance and facilitate the diffusion process; thus allowing the large aromatic molecules to crack into small ones through the acidic center. Corma et al. synthesized NiMo/MCM-41 catalysts for HDT and the results showed that these catalysts were active in comparison to other supports (like USY or precipitated silica–alumina) [18]. These materials have already been tested for mild hydrocracking [18], aromatic hydrogenation [19], and hydrodesulfurization (HDS) of dibenzothiophene and petroleum resides [20,21]. It has been also reported that Mo on MCM-41 is a good demetallation catalyst [22]. However, hydrodesulfurization activities obtained with NiMo catalysts supported on purely siliceous MCM-41 were less than their alumina-supported counterparts [20].

SBA-15 type of ordered mesoporous material, obtained by using a triblock copolymer as structure-directing agent under strongly acidic conditions, has attracted considerable attention in the fields of heterogeneous catalysis and nanoscale materials [23]. SBA-15 possesses a high surface area (600–1000 m^2/g) and is formed by a hexagonal array of uniform tubular channels with tunable pore diameters in the range of 5–30 nm, obviously larger than those of MCM-41 and HMS. The high surface area and controlled pore size of MCM-41 and SBA-15 make them promising supports for application in oil refining. Pore wall thicknesses of around 3–6 nm and 2D hexagonal packing of SBA-15 provide higher thermal stability than displayed by MCM-41, which consists of hexagonal packing of one-dimensional (1D) channels with p6mm symmetry [24]. Compared to MCM-41 type of mesoporous materials, SBA-15 has proven efficient for the HDS of dibenzothiophene (DBT) [25], probably due to their desirable textural properties which enhance the relatively easier access of reactant molecules into its pores; thus increasing the rate of hydrotreating reactions.

Many works have dealt with the preparation of supported and unsupported molybdenum-based catalysts [26,27]. However, the NiW sulfide bulk systems are less studied [28,29]. W-based catalysts are known to have a more hydrogenating character than their Mo counterparts. Thus, it is interesting to analyze the performance of W-based catalysts, in particular W/SBA-15 catalysts, during the HDS and hydrodenitrogenation (HDN) of real feedstocks with high contents of refractory sulfur and nitrogen compounds. These molecules can be efficiently removed mainly via the hydrogenation–desulfurization route.

An enormous amount of knowledge has been accumulated on the crucial role of cobalt and nickel promoters in the course of 90 years. However, very little studies have been done using Fe as a promoter in hydrotreating reactions. In lieu of the deductions made from the study of Mo/MCM-41 catalyst system, which was promoted by Fe and Ni, for HDS of DBT and hydrogenation (HYD) of 2-methylnaphthalene reactions, Linares et al. [30] noted that the incorporation of Fe possibly induced Bronsted acidity that enhanced the performance of such a catalyst. That notwithstanding, in the comparison of typical promoters employed in the preparation of HDT catalysts, one can accede to the fact that the cost of Fe per kilogram is less expensive as compared to Ni and Co counterparts [1]. Hence, one has to consider the economical benefits to be derived when Fe is used as a promoter in the hydrotreating catalyst system formulation.

The aim of this work is to investigate the effect of applying different pore diameter SBA-15 supported FeW catalysts for the hydrotreatment of heavy gas oil derived from Athabasca bitumen. To the best of our knowledge, this type of study has not yet been reported in the literature for real feedstocks. In this investigation, four mesoporous silica SBA-15 supported catalysts with pore diameters in the 5–20 nm range were prepared and have been used for hydrotreating of heavy gas oil (HGO) under industrial process conditions.

2. Experimental

2.1. Preparation of supports and catalysts

The siliceous SBA-15 materials were synthesized using hexanes as a micelle expander under acidic conditions, according to the procedure described elsewhere [31,32]. The triblock copolymer Pluronic P123 (M_{av} = 5800, $EO_{20}PO_{70}EO_{20}$, Aldrich) was used as the structure-directing agent (SDA) and tetraethyl orthosilicate (TEOS) as the silica source. The nominal molar ratio of the chemicals used in the synthesis mixture was $1.0TEOS:0.0168P123:4.02C_6H_{14}:0.0295NH_4F:4.42HCl:186H_2O$. SBA-15 materials with different pore diameters were synthesized by varying the molar ratio of C_6H_{14} and NH_4F. In a typical synthesis procedure, 9.8 g P123 and 0.109 g NH_4F were dissolved in 335 mL of 1.3 M aqueous HCl solution at room temperature. This solution was transferred to a constant temperature bath (CTB) maintained at 15 °C. After 1 h of mechanical stirring, a mixture of 20.8 g TEOS and 34.6 g C_6H_{14} was added. The reaction was allowed to proceed under mechanical agitation for 24 h in the CTB, after which the gel formed was isolated and subjected to hydrothermal treatment in a teflon-lined autoclave for 3 days. The solid product was filtered, washed with deionized water, and dried for 24 h at room temperature. To remove the organic template; the sample was calcined at 550 °C for 5 h using a heating rate of 2 °C/min.

2.2. Synthesis of FeW/SBA-15 catalysts

FeW catalysts supported on SBA-15 with different pore diameters were prepared by an aqueous impregnation technique. The calcined SBA-15 support was impregnated successively using aqueous solutions of ammonium metatungstate (AMT), $(NH_4)_6H_2W_{12}O_{40}$ (Fluka) and iron nitrate, $Fe(NO_3)_3{\cdot}9H_2O$ (Aldrich) as a W and Fe source, respectively. After each impregnation, the catalysts were dried at 100 °C for 24 h. In a typical synthesis, 0.514 g AMT was dissolved in 15 mL de-ionized water until a homogenous solution was formed. 2.55 g siliceous SBA-15 was added to this solution, to get 15 wt.% W/SBA-15. This mixture was dried in an oven at 100 °C. 2 wt.% Fe was also loaded by using same approach. The prepared catalysts are designated as Cat-A, Cat-B, Cat-C and Cat-D with pore diameters 5 nm, 10 nm, 15 nm and 20 nm, respectively.

2.3. Characterization

The calcined SBA-15 samples were characterized by small angle X-ray scattering (SAXS) to ascertain their crystal structures. Diffraction patterns were recorded with a Bruker Smart 6000 CCD detector on a 3-circle D8 goniometer using a Rigaku RU 200 Cu rotating anode generator fitted with parallel focusing cross-coupled mirrors and a 0.5 mm pinhole collimator. Data was obtained using a still data collection (Bruker Software: SMART) with an exposure time of 300 s in the 0–10.0° range. Broad angle XRD patterns of all the SBA-15 supported catalysts were recorded on a Rigaku diffractometer using Cu Kα radiation.

Nitrogen physisorption isotherms were measured on a Micromeritics ASAP 2000 analyzer at liquid nitrogen temperature