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Hydroprocessing of heavy gas oils using FeW/SBA-15 catalysts: Experimentals, optimization of metals loading, and kinetics study

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ABSTRACT

In the present work, a series of FeW/SBA-15 catalysts were prepared and screened for their hydrodesulfurization and hydrodenitrogenation activities using bitumen-derived heavy gas oil from Athabasca. A systematic process optimization study has been conducted to investigate the optimum process conditions required to evaluate kinetic parameters for these reactions. Catalyst metal loadings were varied from 0 to 5 and 15 to 45 wt.% for Fe and W, respectively; resulting in an optimum catalyst (Cat-5) with metal loadings of 3.0 and 30.0 wt.% for Fe and W, respectively. Several techniques were employed to characterize the prepared catalysts and activity results have been correlated with that obtained from characterization. Hydrotreating experiments were performed in a continuous flow micro trickle-bed reactor at the temperatures, pressures, and LHSVs of 633–693 °K, 7.6–9.6 MPa, and 0.5–2 h^{-1}, respectively, with H_2 flow rate and catalyst weight maintained constant at 50 mL/min and 1.5 g, respectively, in all cases. Three kinetic models were applied to fit experimental data obtained from HDS and HDN reaction studies evaluated within temperature range of 633–693 °K. The optimum operating conditions for maximum sulfur and nitrogen conversions occurred at temperature, pressure, and LHSV of 673 °K, 8.8 MPa, and 1 h^{-1}, respectively. Experimental data fitted with the Power Law model yielded reaction orders of 2.0 and 1.5 for HDS and HDN reactions, respectively; and activation energies of 129.6 kJ/mol and 150.6 kJ/mol, respectively. By fitting a modified power law model (Multi-parameter model) to the kinetic data yielded hydrodesulfurization (HDS) and hydrotreating (HDN) reactions orders of 2.2 and 1.8, with respective activation energies of 126.7 kJ/mol and 118.8 kJ/mol.

1. Introduction

Mounting worldwide concern to meet the increasingly stringent regulations on transportation fuels such as diesel and gasoline have explored deep hydrodesulfurization (HDS) under severe conditions [1–3], and utilization of better catalysts for gas oils hydrotreatment [4]. Indeed, hydrotreatment targets the removal of heteroatomic species (S, N, etc.) and also aims to minimize the detrimental poisoning effect of catalysts used in downstream refinery processes. By virtue of the growing demand on quality light to middle distillate oil fractions, catalytic hydroprocessing of heavy oil fractions continues to provide benefit to the modern petroleum refinery. As a result, extensive effort has been attributed worldwide toward characterizing such heavy oil fractions from the standpoints of feedstock properties and the resultant kinetic properties [5–7]. In lieu of this, for instance, the maximum permissible sulfur content in diesel fuels is now targeted to the ultra low levels (10–15 ppm) [8–10]. Thus, the development of highly active and selective HDS catalysts, capable of processing low quality heavier feedstocks, is a pertinent challenge encountered by the petroleum industry of recent times.

In the conventional hydrotreating (HDT) process, compounds containing heteroatoms such as organic sulfur and nitrogen undergo surface catalytic reactions with pre-adsorbed hydrogen to form hydrogen sulfide and hydrocarbon [11,12]. Commercially used catalysts to perform HDT reactions are typically composed of sulfides of molybdenum or tungsten (10–20 wt.%) supported on γ-Al_2O_3, and mostly promoted by either cobalt or nickel (3–5 wt.%) [13–16]. The catalytically active phase formed thereof in a promoted Co (Ni) Mo sulfide catalyst system is the so-called CoMoS or NiMoS phase, in which the promoter atoms (Ni or Co) decorate the edge of well-dispersed MoS_2 nanoparticles on the support [14,17]. Due to tighter environmental regulations regarding sulfur reduction in fuels, researchers and refineries need to develop much higher performance catalysts for HDS [12,16]. In this regard, numerous studies have been conducted on the development of new catalyst systems with greater activity than the current industrial catalysts. Strategies employed to achieve this goal include

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active phase formulation, new preparation methods, and variation or modification of the catalyst support [16,18–22].

Catalytic performance improvement via the option of support modification has been found to be very crucial [20,23]; thus, contributing immensely to the overall HDT activity. Potential catalyst supports that have been investigated over the years include carbon-based materials [24,25], mixed oxides [26,27], zeolites [28] and ordered mesoporous silica materials like MCM-41 [29,30], HMS [22,31], KIT-6 [32,33], and SBA-15 [16,34]. The latter catalyst support has garnered significant attention in the field of heterogeneous catalysis and related fields of nano-materials syntheses due to its attractive textural properties. SBA-15 is characterized by its high surface area (600–1000 m^2/g), high hydrothermal stability and uniformly distributed hexagonal array of cylindrical pore channels with tunable pores in the range of 5–30 nm [35,36]. In addition to its high thermal and hydrothermal stability [37,38], it is conceivable that the large and ordered pore diameter of SBA-15 would enhance the relatively easy access of reactant molecules into the pores; thus increasing the rate of HDT reactions. Furthermore, SBA-15 with relatively large pore diameters could be envisaged to minimize the effects of catalyst coking by pore mouth blocking, which is profound with γ-Al_2O_3 support during the HDT reactions [39]. Moreso, the high surface area of SBA-15 would enhance great dispersion of supported metals so as to increase the amount of catalyst metals converted from the oxide phase to the sulfide phase. These attractive properties of SBA-15 made it a potential worth exploring in real feedstock hydrotreatment applications [16].

In the hydrodesulfurization of dibenzothiophene and the hydrogenation (HYD) of toluene using pure SBA-15 supported NiW-S catalyst, Vradman et al. reported an increased catalytic activity of the order of 1.4 and 7.3 times higher, respectively, than that of the sulfided commercial $CoMo/Al_2O_3$. Their findings evidenced the excellent potential of high loading sulfided NiW/SBA-15 catalysts for deep hydrotreatment of real petroleum feedstocks [40]. Also, Dhar et al. evaluated the catalytic performance of purely siliceous SBA-15 supported Mo, CoMo, and NiMo catalysts for the HDS of thiophene and HYD of cyclohexene, and correlated the catalytic activities with the quantity of oxygen chemisorbed on the vacancies of the respective sulfided catalysts [34]. The good correlation found between the catalytic activities and oxygen chemisorption was attributed to the formation of a patchy monolayer as a result of oxygen chemisorption at the anionic vacant sites of the MoS_2 catalysts. An activity comparison with γ-Al_2O_3-supported catalysts clearly indicated the SBA-15-supported catalysts to be superior to its γ-Al_2O_3 counterpart prepared in similar manner. Nonetheless, the aforementioned limited number of studies in which pure SBA-15 was applied as a catalyst support for HDT reactions employed model compounds as the feedstocks [34,40]. However, a study conducted by Sundaramuthy et al. tested the catalytic functionality of AlSBA-15-supported NiMo catalyst by screening with a light gas oil (derived from Athabasca bitumen) petroleum fraction. The catalyst with 17 wt.% Mo and 3.4 wt.% of Ni was found to produce the best HDN and HDS activities, which was comparable to the conventional γ-Al_2O_3-supported NiMo catalyst at industrial conditions [41].

It is worth mentioning that notable among the aforementioned studies using SBA-15 catalyst support [34,40,41], is the fact that the pore diameters of the supports varied in the range of 5–8 nm. However, in the HDT of heavier petroleum fractions, it is generally more practicable to use catalysts with larger pore diameters so as to enhance efficient species diffusion and also to minimize the possibilities of pore-plugging via coke deposition [39]. Even though our previous investigations on the effectiveness of different pore diameter FeW/SBA-15 catalyst concluded that the catalyst with pore diameter of at least 10 nm was superior amongst the catalysts studied for the hydrotreatment of bitumen-derived heavy gas oils, 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 [16], one should note that the potential industrial application of such catalyst systems would require thorough kinetic studies.

Several kinetic studies documented in the open literature on hydrotreating reactions using real feedstocks have mostly used the Power Law model [42–46], Langmuir–Hinshelwood model [45–47], and Multi-parameter model [42,46] to determine significant kinetic parameters. It is well known that in the hydrotreating processes, adsorption of reactant species on the catalyst active sites is known to be the rate-determining step in the reaction process [48]. It also noteworthy that hydrogen sulfide tends to adsorb strongly on the catalyst active sites; thus, inhibiting the adsorption of nitrogen and other sulfur molecules during hydrotreating [47,48]. One would therefore expect that the Langmuir–Hinshelwood and the Multi-parameter models which account for such inhibition contributions during the HDT process would be more representative and thereby preferred for kinetic analyses in the HDS and HDN of real feedstocks.

The present study is an extension of our previous investigations on the effectiveness of different pore diameter FeW/SBA-15 catalyst [16]. The principle goal of this study is to investigate the optimum process conditions required for the HDT of heavy gas oils using a series of prepared FeW/SBA-15 catalysts, and also to conduct kinetic studies using the Power Law, Langmuir–Hinshelwood, and Multi-parameter models to ascertain the effects of process variables on the rates of HDS and HDN reactions in a way to provide in-depth understanding of HDT reactions as they occur on heterogeneous FeW/SBA-15 hydrotreating catalysts.

2. Experimental

2.1. Preparation of supports and catalysts

In the synthesis of the siliceous SBA-15 materials, the procedure described in our previous paper was followed [16,36], using a triblock copolymer Pluronic P123 (M_{av} = 5800, $EO_{20}PO_{70}EO_{20}$, Aldrich) 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 $1.0TEOS:0.0168P123:4.02C_6H_{14}:0.0295NH_4F:4.42HCl:186H_2O$. 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 288 °K and a mixture of 20.8 g TEOS and 34.6 g C_6H_{14} was slowly added under vigorous mechanical stirring. After 24 h of mechanical agitation of the content in the CTB, 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. The organic template was then removed by calcining the powdered sample at 823 °K for 5 h at a heating rate of 2 °K/min.

2.2. Synthesis of FeW/SBA-15 catalysts

The series of SBA-15 supported FeW catalysts were prepared by an incipient wetness 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, $Fe(NO_3)_3.9H_2O$ (Aldrich) as a W and Fe source, respectively. After each impregnation, the catalysts were dried at 373 °K for 24 h. To prepare the catalyst with 2 and 15 wt.% Fe and W, respectively, 2.55 g of the pristine SBA-15 support was added to a homogenous solution made by dissolving 0.514 g AMT in 15 mL de-ionized water. This mixture was dried in an oven at 373 °K for 24 h and the required amount of Fe was also loaded by a similar