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Application of multi-walled carbon nanotubes as efficient support to NiMo hydrotreating catalyst

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Abstract

The feasibility of multi-walled carbon nanotubes (MWCNTs) as support to NiMo catalysts for hydrotreating of gas oil derived from Athabasca bitumen was tested in a trickle bed reactor at industrial conditions. High quality MWCNTs were prepared by CVD method using ferrocene as catalyst and toluene as carbon source. The produced MWCNTs were characterized by XRD, TEM, TGA and Raman spectroscopy in order to reveal the morphological and structural characteristics. Using functionalized MWCNTs as support, NiMo catalysts were prepared with varying Ni and Mo content by pore filling impregnation method. The calcined NiMo/MWCNTs catalysts were characterized by ICP-MS, N_2 adsorption, XRD and TPR and the sulfide form of the catalysts was examined by DRIFT spectroscopy of adsorbed CO. The XRD patterns confirm the enhanced dispersion of MoO_3 particles when increasing the Ni content from 0 to 4.5 wt.% over 12 wt.% Mo/MWCNTs. The TPR profiles indicate the two step reduction characteristics of Mo^{6+} to Mo in lower oxidation state such as Mo^{4+} and Mo^0. The promoted and unpromoted MoS_2 sites were clearly differentiated with the help of DRIFT of adsorbed CO over sulfided catalysts. The number of Ni promoted MoS_2 (NiMoS phase) sites is increased significantly with increasing Ni addition up to 3 wt.% over 12 wt.% Mo/MWCNTs. The HDN and HDS activities of sulfided NiMo/MWCNTs using bitumen derived light gas oil were carried out at different temperatures under industrial condition. The HDN and HDS activities of the catalysts increased with increasing Ni content up to 3 wt.% and Mo content up to 12 wt.%. Based on weight of the catalyst, the HDN and HDS activities of 3 wt% Ni–12 wt.% Mo/MWCNTs are significantly higher than those over conventional Al_2O_3-based catalyst under the experimental conditions studied. The introduction of 2.5 wt.% P to MWCNTs-based catalyst found to show a fall in hydrotreating activity.

Keywords: Multi-walled carbon nanotubes; NiMo catalyst; DRIFT of adsorbed CO; Hydrotreating; Light gas oil; NiMoS phase

1. Introduction

Hydrotreating is an important crude oil refining process that removes N and S containing hydrocarbon molecules from gas oil by reacting them with H_2 over a catalyst. Developments in petroleum refining are moving in a direction to produce clean fuels with less than 15 ppm of sulfur. This is a challenging task. It is reported that to bring the sulfur level from present 500 to 15 ppm level needs catalysts, which are ∼7 times more active than the existing ones [1]. This urgent need of drastic reduction of the sulfur level in transportation fuels motivated the search for novel and more efficient catalysts. Industrial hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes have been largely carried out over sulfided Mo-based catalysts promoted with Ni or Co, supported on γ-alumina [2,3]. γ-Alumina is the most widely used support material for preparing commercial hydrotreating catalysts due to its good mechanical and textural properties. Notable features of alumina support include their ability to provide high dispersion of the active metal components [4]. However, a major drawback of alumina is its strong chemical interactions that exist between the amorphous Al_2O_3 and transition metal oxides from precursors in the catalyst preparation step, which makes the complete sulfidation of supported metal oxides difficult. There are number of approaches, like changing the active component, varying the preparation method and changing the support, to prepare better catalysts with enhanced

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activity in hydrotreating of gas oils. Supports such as clays [5], zeolites [6], oxides such as SiO_2 [7], TiO_2, ZrO_2 [8–10], and carbon [11] and several combination of metal oxides [12] have been studied in detail as support to NiMo and CoMo catalysts for hydrotreating of various gas oils and model compounds.

Recently, the attention is shifted to mesoporous materials like MCM-41 [13], HMS [14] and siliceous and transition metal substituted SBA-15-based systems [15–16]. In the carbon-based supports, new forms of carbon nanomaterials such as carbon nanotube (CNT), fullerene nanotube (FNT) and carbon nanosphere (CNS) are considered as important nanomaterials due to their potential application in many fields in nanotechnology and few attempts have been made to use them in catalysis. Among the above carbon allotropes, multi-walled carbon-nanotubes (MWCNTs) are drawing increasing attention recently as a novel support material in catalysis and number of reports appeared in open literature [17,18]. The catalytic applications involve selective hydrogenation [19], hydrofomylation [20], selective dehydrogenation [21], ammonia synthesis [22], Fischer-Tropsch synthesis [23], methanol synthesis [24] and higher alcohol synthesis [25]. Dong et al. [26] studied the usage for MWCNTs as support to Co–Mo sulfide catalyst for HDS of thiophene. They found a significant increase in the molar percentage of catalytically active Mo species in the total Mo-amount and hence pronounced enhancement of the reversibly adsorbed hydrogen at the surface of the functioning catalyst, resulting in a significant increase in HDS activity. Shang et al. [27] compared that HDS activities of oxide state of Mo, Co–Mo and sulfide state of Mo on CNTs and Al_2O_3 and found that the main active molybdenum species in the oxide state MoO_3/CNTs catalysts was MoO_2, rather than MoO_3 as generally expected. The HDS of DBT showed that Co–Mo/CNTs catalyst was more active than that of Co–Mo/Al_2O_3 and the hydrogenolysis/hydrogenation selectivity of Co–Mo/CNTs catalyst was also much higher than Al_2O_3-based catalyst. Further, catalyst with Co/Mo atomic ratio of 0.7 showed the higher activity. The effect of surface modification of MWCNTs with HNO_3 on HDS activity of Co–Mo/MWCNTs was studied and found that the dispersion of Co–Mo on MWCNTs improved significantly after the modification by acid treatment [28]. Even though there are number of reports on MWCNTs in catalysis, none of the studies have targeted the Ni–Mo-related catalysts for the hydrotreating of gas oil derived from Athabasca bitumen at industrial condition. Hence, in the present work, highly active MWCNT supported NiMo sulfide catalysts were prepared and their catalytic performances in HDN and HDS of light gas oil (LGO) derived from Athabasca bitumen are evaluated, and compared with the reference system based on conventional Al_2O_3 under similar experimental conditions. Also, the effect of P addition to NiMo/MWCNTs catalyst on hydrotreating activity was studied.

2. Experimental

2.1. Synthesis and purification of MWCNTs

High quality MWCNTs were synthesized by CVD method using ferrocene as catalyst and toluene as carbon source in a tubular quartz reactor. The detailed experimental procedure is given in our earlier report [29]. The MWCNTs were produced at 800 °C with Fe/C ratio of 0.45 with residence time of 15 s. The as-grown CNT product was purified by treating with 5 M HCl (50 ml/g) under reflux condition for 24 h. The purified MWCNTs were treated with 52% nitric acid and refluxed for 8 h in order to create various functional groups in the surface of MWCNTs, which are highly beneficial in preventing the leaching of Ni and Mo particles during the reaction. The filtered MWCNTs product was then washed several times with deionized water and dried at 110 °C for 24 h.

2.2. Characterization of MWCNTs support

The morphological as well as structural features of the purified MWCNTs were analyzed by SEM, TEM, XRD and Raman spectroscopy. The SEM image of the MWCNTs was recorded in JEOL 840A SEM instrument. The CNTs sample was first coated with gold and used for scanning. Similarly, the microstructure of MWCNTs was studied by TEM using Philips CM 12 instrument. The MWCNTs sample was dispersed in acetone by sonication and a drop of the sample was placed over a holey carbon coated copper grid and subjected to imaging. Using Rigaku XRD instrument with Cu Kα radiation ($\lambda = 0.1541$ nm) and Ni filter, the XRD pattern of the MWCNTs sample was recorded in the 2θ range 20–50° with a scan rate of 0.05°/s. The vibrational modes of MWCNTs were measured in the range of 1000–2000 cm^{-1} using Raman spectrometer (Renishaw) equipped with a Nd:YAG laser source.

2.3. Synthesis and characterization of NiMo/MWCNTs catalysts

Using the functionalized MWCNTs as support, NiMo catalysts with varying Ni and Mo contents were prepared by pore filling wet impregnation method. The functionalized MWCNTs were first impregnated with required amount of aqueous ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] solution and dried at 120 °C for 4 h. The dried materials were calcined at 450 °C for 5 h in air. Then, the Mo/MWCNTs were impregnated with required amount of aqueous $Ni(NO_3)_2$, dried and calcined at 450 °C for 5 h in air obtain NiMo/MWCNTs catalyst. The Mo and Ni contents were varied as 0, 5, 12 and 20 wt.% and 0, 1.5, 3.0 and 4.5 wt.%, respectively. Similarly, using conventional Al_2O_3 as support, 3 wt.% Ni–12 wt.% Mo catalyst was prepared for comparison purpose. The effect of order of impregnation of Mo and Ni over MWCNTs was studied with 3 wt.% Ni and 12 wt.% Mo over MWCNTs prepared by impregnating Ni first followed by Mo following the same procedure (3 wt.% Ni–12 wt.% Mo/MWCNTs*). In order to study the effect of addition of phosphorus promoter, 2.5 wt.% P was loaded over 3 wt.% Ni–12 wt% Mo/CNTs by co-impregnation method. The support was impregnated with an aqueous solution (pH ~4) containing the appropriate amounts of ammonium heptamolybdate (99.9%, Aldrich), nickel nitrate (99%, BDH) and phosphoric acid (AnalaR, BDH) and dried at 120 °C for 5 h before calcination at 450 °C for 5 h in air. The