Preparation of Ni-Mo₂C/carbon catalysts and their stability in the HDS of dibenzothiophene

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ABSTRACT

The HDS activity and stability of Ni-Mo₂C/AC catalysts, prepared by carbothermal hydrogen reduction (CHR) at different temperatures and with different Ni:Mo ratios, is reported. The highest HDS activity occurred for catalysts with Ni:Mo ratios of 0.38 and 0.19, when prepared at the relatively low CHR temperature of 550 and 600 °C, respectively. Partial sulfidation of the Ni-Mo₂C/AC catalysts occurred rapidly upon reaction in 2 wt% dibenzothiophene (DBT) at 350 °C and 2.1 MPa H₂. Uptake of S was enhanced with increased Ni content, resulting in the formation of Mo₂C-MoS₂ core-shell structures. The stack height of the MoS₂ shell increased with increased Ni content and promoted the direct desulfurization of DBT.

1. Introduction

Hydrodesulfurization (HDS) [1] is an important processing step in heavy oil upgrading that uses NiMoS/Al₂O₃ or CoMoS/Al₂O₃ catalysts to facilitate S removal from heteroaromatic compounds present in the heavy oil [2,3]. Novel catalysts, such as metal carbides and nitrides, have also been investigated as potential hydrotreating catalysts over the past several decades [4–6], in part because of their noble metal-like catalytic properties [7–10]. Sajkowski and Oyama [11] reported that a Mo₂C/Al₂O₃ catalyst had twice the HDS activity of a conventional MoS₂ catalyst when measured at 633 K and 13.0 MPa H₂ using a gas oil with 116 ppm S. The comparison was made based on the number of active sites as measured by CO uptake. Similarly, Da Coasta et al. [12] reported that a Mo₂C/Al₂O₃ catalyst doped with P was more active than an industrial hydrotreating catalyst for aromatics hydrogenation, HDS and hydrodenitrogenation (HDN) when measured at industrial conditions (613 K, 3 MPa) using a gasoil with 47 ppm S content.

One of the difficulties encountered when applying Mo₂C catalysts for HDS is that they are unstable because of surface sulfidation, even in the presence of low concentrations of S (< 0.1 wt%). Aegerter et al. [13] proposed that a thin layer of highly dispersed MoS₂ is formed on the surface of Mo₂C or Mo₂N particles during thiophene HDS, as evidenced by IR and TPD-CO characterization of the catalysts. The authors proposed that Mo₂C and Mo₂N particles serve as rigid substrates for a sulfided Mo phase, exposing a large number of co-ordinatively unsaturated (cus) Mo sites, which results in increased activity of the catalyst (by 50%), compared to a conventional MoS₂ catalyst. Da Costa et al. [14] also reported that a Mo₂C catalyst became

more active than a Co-Mo/Al₂O₃ commercial catalyst for the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) with low levels of S in the feed (< 135 ppm). Oyama et al. [15] suggested the formation of a Mo-carbosulfide active site to explain product selectivities observed during the simultaneous conversion of sulfur, oxygen and aromatic compounds over Mo₂C, compared to the product selectivities measured with a single reactant, especially for the case of cumene hydrogenation. In another study, Brito and coworkers [16] presulfided a NiMo carbide catalyst prior to HDS and claimed that a Ni-Mo-S phase was responsible for the measured HDS activity. Guangzhou et al. [17] reported on NiMo carbide and Mo₂C catalyst performance for the HDS of dibenzothiophene (DBT) and pointed out that Ni addition increased the Mo₂C activity by 57%, although there was no conclusion drawn regarding the effect of S on the metal carbides during HDS. The transformation of Mo₂C catalysts in the presence of S-compounds remains somewhat unclear and the application of these catalysts for HDS in high S concentrations (as is the case for gas oils derived from residue oils, for example) has not been reported.

Several methods have been developed to synthesize Mo₂C catalysts, either as bulk, unsupported catalysts or as Mo₂C dispersed on high surface area Al₂O₃ [13] and carbon supports [18,19]. The most common synthesis method uses temperature-programmed reduction (TPR) of metal oxides in mixtures of H₂ and a hydrocarbon such as CH₄ [20] or C₂H₆ [21]. However, the resulting low surface area and carbon residue on the catalyst surface means that the catalysts have relatively low activity. An alternative preparation method uses carbothermal hydrogen reduction (CHR), employing a carbon support and pure H₂ to generate the metal carbide at high reduction temperatures

(700–800 °C). This method yields nanoparticles of Mo_2C, as first demonstrated by Mordenti et al. [22] and Liang et al. [23] and also reported previously by the authors [24]. Thus, CHR is a relatively facile method to synthesize carbon supported Mo_2C catalysts, in which the carbon support may also suppress coke formation during residue oil upgrading [25]. However, CHR has a limited capacity to achieve complete reduction/carburization of the catalyst precursor, even at high reduction temperatures. For example, in previous work [24], CHR of ammonium heptamolybdate impregnated activated charcoal (AC) yielded a mixed Mo_2C/MoO_xC_y phase with a relatively high portion of Mo_2C (~50%) obtained at 700 °C. However, almost half of the carbon support was hydrogenated (mostly to CH_4) during the CHR process, which decreased the support area available to achieve high dispersion of the Mo_2C.

One potential option to increase the Mo_2C dispersion is to add a second metal to decrease the synthesis temperature required for the formation of the metal carbide. Liang et al. [26] reported that the presence of Co decreased the CHR temperature for Mo_2C formation to 600 °C, at a Co/Mo molar ratio of 1.0. They concluded that the Co increased the formation of CH_x species during CHR, facilitating carburization of the Mo. Similar effects have been reported in the synthesis of W_2C by CHR using Ni as the promoter [27,28]. The presence of the 2nd metal has also been shown to provide synergistic effects in the case of Co added to Mo_2C when used for the chemo-selective reduction of nitroarenes, with the $Co-Mo_2C/AC$ catalyst having significantly higher activity than the Mo_2C/AC alone [29]. Moreover, the bimetallic carbides formed in the presence of Mo and other transition metals [30,31] such as Fe, Co and Ni, show effective catalytic activity in hydrotreating reactions.

The present study reports on the CHR synthesis of $Ni-Mo_2C$ supported on activated carbon (AC) and their application to the HDS of DBT at high S concentrations (~3500 ppm) that mimic the S content of heavy oil [1]. New data are reported that capture the effect of Ni content on the formation of the $Ni-Mo_2C$ catalysts and their resulting HDS catalytic activity. In particular, the changes in catalyst morphology that occur during reaction, with the formation of a core-shell MoS_2-Mo_2C structure, is reported for the first time. The structural changes are related to the stability of the $Ni-Mo_2C/AC$ and the Mo_2C/AC catalysts.

2. Experimental

2.1. Catalyst preparation

Activated charcoal (AC: 1025 m^2/g, pore volume 0.85 mL/g) was impregnated with a solution of ammonium heptamolybdate (AHM) in acetone (10%) and H_2O (90%) and rotary evaporated under vacuum to remove all the solution. The resulting solid was aged in air for 4 h before drying at 110 °C overnight to yield the precursor. The precursor was then calcined in N_2 at 300 °C for 5 h to obtain the oxide states of Mo, Ni or bimetallic NiMo. The calcined precursor (ca. 1.8 g) was placed in a U-tube reactor and subsequently converted to the $Ni-Mo_2C/AC$ catalyst by CHR in a continuous H_2 flow (200 mL (STP)/min), while increasing temperature from room temperature to 500 °C at 10 °C/min, followed by increasing temperature at 1 °C/min to 650 °C and holding the final temperature for 90 min before quenching to room temperature in N_2 [24]. This catalyst (designated as 10%Mo_2C/AC-650) was compared with $Ni-Mo_2C/AC$ catalysts, prepared similarly but with successive impregnations of the AC with solutions of AHM and Ni $(NO_3)_2$, respectively, to obtain precursors with different Ni:Mo ratios. After calcination, the precursors were converted to $Ni-Mo_2C/AC$ by CHR as described above but with final reduction temperatures of 550 °C or 600 °C. The resulting $Ni-Mo_2C$ catalysts with different Ni:Mo ratio (from 0.02–0.76) are designated as Ni_xMo_2C-y, where x represents the Ni:Mo atomic ratio and y represents the reduction temperature (°C). The 10% Mo_2C/AC-650 and $Ni-Mo_2C/AC$ catalysts, used in the batch reactor to determine reaction kinetics, were loaded into the batch

reactor without passivation. The catalysts were transferred from the preparation U-tube reactor to the batch reactor in a glove bag under a N_2 blanket to ensure minimal air exposure. For the catalyst stability tests conducted in the trickle-bed reactor and for the characterization of the fresh catalysts (XRD, BET), the catalyst samples were first passivated in a flow of 1 vol% O_2/N_2 at room temperature for 2 h prior to the analysis and a mild pre-reduction of the passivated catalysts was done prior to the reaction test. Carbon supported MoS_2 (MoS_2/AC) was also used herein as a reference to compare with the used $Ni-Mo_2C/AC$ catalysts. The MoS_2/AC precursor was prepared similarly to the Mo_2C/AC precursor followed by ex-situ presulfiding in a 100 mL decalin for 3 h at 350 °C under approximately 10 vol% H_2S/H_2 generated from CS_2 (with further details provided in the Supporting information).

2.2. Catalyst characterization

Elemental analysis of the catalysts was conducted by inductively coupled plasma atomic emission spectroscopy (ICP-OES). All samples were acid digested in aqua regia at 110 °C to extract all metals from the support, prior to the analysis. The adsorbed S on the used catalysts was determined using a Perkin-Elmer 2400 series II CHNS/O Analyzer. The combustion temperature was set at 975 °C.

The Brunnauer-Emmett-Teller (BET) surface area, pore volume and pore size of the calcined $Ni-Mo_2C$ precursors, passivated $Ni-Mo_2C$ and used catalysts (following HDS reaction) were determined from N_2 adsorption/desorption isotherms measured at −196 °C using a Micromeritics ASAP 2020 analyzer. The used catalysts were washed with acetone several times before analysis to remove the decalin solvent used in the reaction. About 0.1 g of the sample was degassed at 200 °C (100 μm Hg) for 4 h prior to the measurement. The BET surface area was calculated from the adsorption isotherm in the relative pressure range (P/P_o) of 0.01–0.20. The total pore volume (V_{total}) was obtained based on the total N_2 adsorption measured at P/P_o = 0.99. The micropore volume (V_{micro}) was obtained by the t-plot method using data measured in the range of P/P_o = 0.18-0.50. The mesopore volume was calculated from the desorption isotherm and the average pore diameter was calculated assuming a cylindrical pore such that d_{pore} = 4 V_{total}/S_{BET}.

A Bruker D8 Focus (0–20, LynxEye detector) diffractometer was used to identify the bulk phases of the synthesized passivated catalysts using a Co Kα (λ = 1.789 Å) radiation source. The instrument was operated at 35 kV and 40 mA in a scan range of 2Θ = 5–90° with a step size of 0.04° and scan speed of 0.5 s/step. After background subtraction, phase identification was processed using standard software. The XRD of the fresh and used catalysts were compared to identify bulk phase changes of the catalysts during reaction.

X-ray photoelectron spectroscopy (XPS) analysis was conducted using a Leybold Max200 spectrometer for surface analysis of the used catalysts. Mg Kα was used as the photon source generated at 1253.6 eV. For a survey scan, the pass energy was set at 192 eV; for a narrow scan, it was set at 48 eV. The C 1 s peak was taken as the reference peak at 284.5 eV to account for charging effects. Exposure of the samples to the atmosphere prior to analysis was minimized to less than 5 min.

Transmission electron microscope (TEM) images of the supported catalysts were generated using a (JEOL) JEM 2200FS electron microscope operated at 200 kV, with a 1.9 Å point-to-point resolution. Used catalysts were analyzed to identify the particle size distribution and characteristic slabs of the synthesized/formed species. The samples were prepared by dispersion in ethanol and then sonicated for several minutes. A drop of the suspension was placed on a 230 mesh copper grid coated with Formvar-Carbon film and then dried in a vacuum chamber. The clusters/particles identified in the TEM images were measured and counted to yield a size distribution that was fitted to a lognormal distribution to determine the average size of the cluster/particle. The number of formed MoS_2 layers was also counted based on the TEM images and the stacking degree (N) of MoS_2 was calculated as