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Experimental study on two-stage catalytic hydroprocessing of middle-temperature coal tar to clean liquid fuels

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ABSTRACT

Special Mo–Co/γ-Al_2O_3 and W–Ni/γ-Al_2O_3 catalysts with different metal loadings were prepared applying new synthesis technologies that combine ultrasonic-assisted impregnation and temperature-programming methods. Clean liquid oil was obtained from middle-temperature coal tar via hydrogenation in two-stage fixed beds filled with the laboratory made catalysts. The Mo–Co/γ-Al_2O_3 catalyst with 12.59 wt.% Mo and 3.37 wt.% Co loadings, and the W–Ni/γ-Al_2O_3 catalyst with 15.75 wt.% W and 2.47 wt.% Ni loadings were selected. The effects of pressure and liquid hourly space velocity on hydrogenation performance were investigated while other experimental conditions remained constant. Gasoline ($\leqslant$180 °C) and diesel (180–360 °C) fractions were separated from the oil product and analyzed. The two-stage reacting system was capable of removing nitrogen and sulfur from 1.69 and 0.98 wt.% in the feed to less than 10 ppm and 100 ppm, respectively in the products. The results indicated that the raw coal tar could be considerably upgraded through catalytic hydroprocessing and high-quality fuels were obtained.

1. Introduction

In view of growing concerns about the petroleum depletion crisis and rising fuel price, major efforts are being dedicated to the development of various usable energy sources to ensure energy security. China is one of the largest coal producers in the world and extensive studies have been focused on the fuel production from coal [1–4]. Abundant coal tar has been produced every year during coal carbonization and gasification [5]. The coal tar can be used as an alternative source for producing conventional liquid fuels (e.g., gasoline and diesel) through its hydrogenation. On the other hand, liquid fuel production is currently subject to strict environmental standards for transport liquid fuels and refractory feeds for refiners [6]. Environmental and economic benefits are inevitably linked to the hydroprocessing of coal tar to produce clean transport fuels with ultra-low heteroatom content.

Coal tar is a complex mixture consisting of aliphatic, aromatic, alicyclic, and heterocyclic compounds. The complexity of coal tar has driven researches that focused on a pure model compound, such as naphthalene [7–10], phenanthrene [10], anthracene [11], and quinoline [12], rather than on a real fraction. Extensive investigations on thermodynamics and kinetics have been performed [13–16]. Detailed reviews of studies on the reaction networks have been provided by Girgis and Gates [17]. The kinetics of the removal of sulfur compounds and other impurities has a critical effect on the optimization of process variables and the selection of catalyst for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) processes [6]. Although studies described above are helpful in understanding the behavior of certain compounds under hydroprocessing conditions, an overall picture of coal tar hydrogenation was not provided. At the temperature and pressure required for hydrotreatment, many undesirable reactions including dehydrogenation, polymerization, isomerization, and condensation would occur [18].

The performance of hydroprocessing units is greatly influenced by the catalyst, type of reactor, process flow, and operating parameters. Physical properties such as the density, porosity, size, and shape of a catalyst are crucial parameters in hydroprocessing heavy feeds [19]. These parameters are feed dependent [20], implying that for certain coal tar feedstock, catalysts with special properties (usually high BET surface and large pore volume) are required. Mo–Co supported on alumina has long life, and under suitable conditions, enables the removal of a high degree of sulfur with little more than theoretical hydrogen consumption [21]. Also, in the study by Raje et al., the hydrotreatment of coal-derived naphtha was evaluated over unsupported transition metal sulfide catalysts of Group VIII in the Periodic Table, and ruthenium sulfide (RuS_2) was found to be the most active catalyst for the heteroatom removal [22]. Furthermore, a low loading Ru/zeolite catalyst was believed to exceed the commercial Mo–Co and Mo–Ni catalysts in HDN activity per weight of metal and price [23]. But it showed a much lower HDS activity. Tungsten sulfide has been claimed as an effective catalyst

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for a wide variety of hydrocarbon reactions including the hydrogenation of olefins and aromatics, and isomerization of naphthenes and paraffins, as well as hydrocracking and hydrogenolysis [24]. It is believed that creating smaller particles of active metals will improve the catalysts' activity. Some recent studies [25–28] have discussed the synthesis of highly dispersed γ-Al_2O_3-supported Mo–Co catalysts using energy from ultrasonic waves.

The present study describes the bench scale two-stage hydroprocessing of middle-temperature coal tar using laboratory made Mo–Co and W–Ni catalysts supported on γ-Al_2O_3 in the first and second stages respectively. Impregnation and temperature-programming technologies were applied to prepare the catalysts. This work primarily aims to reduce heteroatoms (S, N, and O) and produce high-quality liquid fuels under varied reaction pressures and liquid hourly space velocities (LHSV). The coupling of hydrofining for initial hydrogenation in the first stage and hydrocracking for further hydrogenation and C—C bond cracking in the second stage showed promising results.

2. Experimental

2.1. Catalyst preparation and characterization

Hydrofining catalysts (Mo–Co/γ-Al_2O_3) with different Mo and Co loadings were prepared and the synthesis procedure is described as follows: (1) Pretreatment. The commercial γ-Al_2O_3 granules of 20–40 mesh were used as the catalyst support. Higher surface area of the alumina granules was obtained after they were dipped in the 5 wt.% diluted HCl solution for 20 min. Then they were dried at 110 °C for 2 h to get rid of the surface water, after which they were calcined at 500 °C for 6 h to eliminate the water absorbed in the pores and stabilize the framework of the alumina. (2) Ultrasonic impregnation. The support was impregnated in an aqueous solution containing the required amount of ammonium molybdate [$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$] and cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$] for 12 h. During the impregnation process, ultrasonic vibration with a frequency of 50 kHz was applied. Then the Mo and Co precursors will be highly dispersed on the pretreated γ-Al_2O_3 support using energy from ultrasonic waves. (3) Temperature-programmed treatment. The catalyst was heated in the air atmosphere to the temperature of 200 °C and held for 3 h. Then it was heated to 350 °C at a rate of 5 °C/min and held for 3 h, which was finally heated to 500 °C at a rate of 10 °C/min and held at this temperature for 6 h. The hydrocracking catalysts (W–Ni/γ-Al_2O_3) with different W and Ni loadings were also synthesized under the same procedure using the precursors of ammonium metatungstate hydrate [$H_{40}N_{10}O_{41}W_{12}{\cdot}XH_2O$] and nickel nitrate [$Ni(NO_3)_2{\cdot}6H_2O$].

The amount of various metals present on the catalysts was analyzed using ICP-AES (IRIS Intrepid II XSP, ThermoFisher Co., Ltd.). The BET surface area and pore volume measurements of the catalysts were performed with adsorption equipment (Micromeritics) using N_2 gas. X-ray diffraction (XRD) was performed using a diffractometer (X'Pert PRO MPD, PANalytical Co., Ltd.) with Cu Kα radiation filtered by a graphic monochromator at a setting of 40 kV and 40 mA. High resolution transmission electron microscopy (HRTEM, model: JEM-2100, JEOL Co., Ltd.) was also performed to investigate the structure of the catalysts.

Catalysts with different metal loadings were evaluated in the tests of coal tar hydroprocessing. After preliminary screening tests, the hydrofining catalysts (Mo–Co/γ-Al_2O_3) with 12.59 wt.% Mo and 3.37 wt.% Co loadings, and the hydrocracking catalyst (W–Ni/γ-Al_2O_3) with 15.75 wt.% W and 2.47 wt.% Ni loadings showed better performance than did the other catalysts. Thus, they were finally used in the following experiment.

2.2. Feedstock

The distillate (under 360 °C) of the middle-temperature coal tar was used as feedstock in this study. Some properties of the feedstock are listed in Table 1.

2.3. Reaction system

The hydroprocessing of the coal tar was carried out in a continuous two-stage fixed-beds system. As shown in Fig. 1, the entire reaction system was mainly made up of three units, i.e., the reactant feeding, the hydrogenation, and the product separation and collection units. The reactant feeding unit consisted of a tar supply line and a high-pressure hydrogen supply line. The hydrogenation unit consisted of a preheater, a hydrofining reactor, and a hydrocracking reactor. The middle section of each reactor tube was filled with 30 ml catalyst. The product separation and collection unit included a water cooler, a gas–liquid separator, a lye washer and so on.

2.4. Operating procedure and product analysis

Coal tar hydroprocessing was conducted as follows: (I) Pre-sulfidation of catalysts. The sulfidation of catalysts was performed at P_{H_2} = 6 MPa, LHSV = 1.6 h^{-1}, and H_2/oil ratio = 1000 using 2 wt.% dimethyl disulfide in aviation kerosene and underwent a temperature-programmed procedure. (II) Hydroprocessing tests. All the experimental parameters were set at the respective desired values and the tests were conducted at a duration of 120 h. (III) The overall system was washed with ethanol after each run.

The liquid product was distilled into gasoline (⩽180 °C), diesel (180–360 °C) and residue oil (>360 °C) fractions. The samples of gasoline and diesel fractions were then subjected to the following analyses: (i) determination of distillation range by the Engler distillation method (standard: ASTM D86); (ii) C and H elemental analyses on an Elementar VARIO ELIII (Germany), N and S analyses on KY-3000SN (Jiangsu Jiangyan KEYUAN Electronic Instrument Co. Ltd., standard: ASTM D5453 and D4629); (iii) density on DMA 5000 (Anton Paar, Austria); (iv) research octane number (RON) and anti-knock index (AKI) for gasoline; (v) cetane number and solidifying point for diesel; and (vi) detailed composition determined by capillary column GC–MS analysis (Agilent 6890N with a 30 m × 0.25 mm × 0.25 μm HP-5MS capillary column).

3. Results and discussion

3.1. Catalyst characterization

As shown in Table 2, both the Mo–Co/γ-Al_2O_3 and W–Ni/γ-Al_2O_3 catalysts had a BET surface area of ~200 m^2/g and a pore

Table 1
Properties of coal tar fraction.

Properties	Value
Elemental analysis (wt.%)	
C	84.86
H	8.39
N	1.69
S	0.96
O[a]	4.10
H/C molar ratio	1.19
Distillation range (°C)	
IBP	118
10%	196
50%	261
90%	306
Density (20 °C) (g mL^{-1})	1.0078

[a] By difference.