Full Length Article

Study on catalytic performance of oil-soluble iron-nickel bimetallic catalyst in coal/oil co-processing

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GRAPHICAL ABSTRACT

The schematic of reaction process of oil soluble iron-nickel catalyst in coal/oil co-processing: (1) dispersion; (2) sulfurization; (3) reaction.
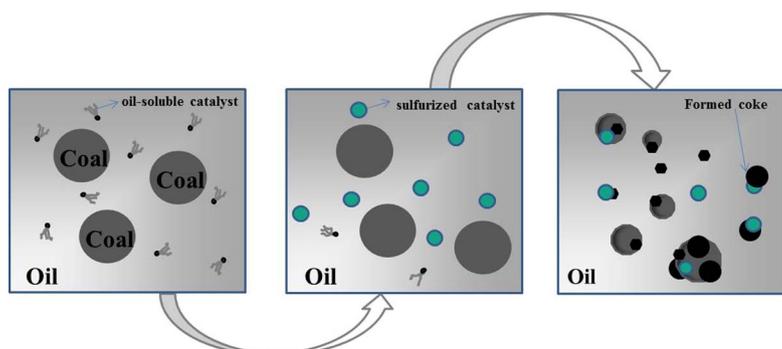
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ABSTRACT

The oil-soluble iron-nickel bimetallic catalyst precursor was synthesized for the application of coal/oil co-processing. The catalyst precursor and its sulfurized product were characterized by FTIR, TG, XRD, and TEM. And the catalytic performance of this catalyst precursor in the coal/oil co-processing system was investigated and compared with the molybdenum naphthenate. The results showed that the average particle size of the synthesized catalyst precursor after sulfurization was about 40 nm, containing $(Fe, Ni)_9S_8$ mixed crystal, and the crystallinity was low with rough edge and large specific surface area. The synthesized catalyst precursor showed better hydrogenation activity compared with the relatively expensive molybdenum naphthenate catalyst. Under the experimental conditions, the yield of coke was only 2.9 wt%, the I value was 6.47, and the conversion yield of dry ash-free coal reached to 90.7 wt%. Characterization and analysis of the coke after reaction further confirmed that the synthesized catalyst precursor could promote the conversion of coal and showed potential application value in coal/oil co-processing.

1. Introduction

Coal/oil co-processing is a kind of direct coal liquefaction technology, which can process coal and heavy oil resources at the same time. This technology can make use of abundant coal resources and residual oil and reduce the pollution caused by the direct combustion of

coal simultaneously [1]. The catalyst used in coal/oil co-processing system can not only reduce the activation energy of the reaction, but also promote the hydrogen transfer [2–4]. Since Bergius firstly proposed the direct coal liquefaction in 1913, the direct coal liquefaction catalyst has been mainly based on molybdenum and iron [5]. Low-cost, highly dispersed iron-based catalysts have been reported in industrial practice, but their lower activities limit the conversion depth of coal liquefaction [6,7].

Therefore, the hydrogenation catalysts with high activities will play an irreplaceable role in increasing coal conversion rate and improving the quality of liquid fuels produced from co-processing. Conventional supported hydrogenation catalysts have been widely used in the traditional direct coal liquefaction techniques, but the poor dispersibility and the pore-plugging problem limited further improvement. In contrast, oil-soluble dispersed catalysts are regarded as promising catalysts, owing to their highly dispersive characteristics in heavy oil and their high ratio of surface area to volume [8,9]. Catalysts for hydrogenation reactions mainly belong to transition metals, especially the molybdenum sulfide as active phases [10]. Nanosized particles of MoS_2 could be well dispersed in the reaction system of coal and heavy oil, and exhibited high catalytic effectiveness for the coal hydrogenation and heavy oil hydrocon-version processes [11]. Trautmann et al. [12] found that the Co/SiO_2 catalyst with its high metal dispersion on a nanostructured support had obviously better effects on the coal conversions compared with the conventional disposable catalyst FeS_2.

Nowadays, due to highly catalytic activities, the oil-soluble molybdenum and nickel-based catalysts are used in coal/oil co-processing, but the high costs limit their application in industry. Correspondingly, the iron-based catalyst has lower activity, but is cheap, environmentally benign, and disposable. There have been several attempts to transplant inexpensive promoters, such as Co, or Fe, into a Mo-based or Ni-based dispersed catalyst, because the addition of a promoter may decrease the cost of the catalyst and enhance its hydrocracking activity [13,14]. The iron-nickel catalysts supported on carbon nanoparticles had shown a high oil yield in direct coal liquefaction [15]. Sang Goo Jeon [8] prepared an oil-soluble CoMo bimetallic catalyst for an application in hydrocracking reaction of heavy oil, which could promote the asphaltene and sulfur conversion activities, maximizing the yield of the liquid product. However, the exploration of combining molybdenum, nickel with iron to prepare oil-soluble catalyst in coal/oil co-processing has not yet been conducted.

In this study, an oil-soluble iron-nickel bimetallic catalyst precursor with fatty acid as organic ligand was synthesized based on a simple method. The chemical structure, thermal stability, active phase composition and micro-morphology of the synthesized catalyst precursor were characterized, and the catalytic performance of synthesized catalyst precursor in coal/oil co-processing was evaluated as well as the molybdenum naphthenate for comparison. Besides, analysis of coke after the reaction were conducted to investigate the effect of synthesized bimetallic catalyst precursor in promoting the conversion of coal during the coal/oil co-processing.

2. Experimental

2.1. Materials

An atmospheric residue from Merey (MRAR) and a kind of coal from Anhui (AHC) were taken as feedstock, and their properties were shown in Table 1. Prior to the experiment, the coal samples were partially dried at 110 °C, and then ground and sieved to particle sizes below 25 μm. All chemicals used in experiments were analytical grade purchased from Sinopharm Chemical Reagent Company (China).

2.2. Preparation of catalysts

Ferric chloride ($FeCl_3$) and nickel nitrate ($Ni(NO_3)_2$) were dissolved

Table 1
Main properties of MRAR and AHC.

properties	MRAR	AHC
density at 20 °C (g·cm^{-3})	0.9976	–
C$_7$-asphaltene (wt%)	10.42	–
conradson carbon residue (wt%)	15.33	–
moisture (wt%)	–	0.75
ash (wt%)	–	3.94
volatile matter (wt%)	–	53.60
fixed carbon (wt%)	–	41.71
C (wt%)	84.82	58.70
H (wt%)	10.87	5.15
S (wt%)	2.89	0.53
N (wt%)	0.63	0.51
O (wt%)	–	35.29
H/C atomic ratio	1.54	1.05

in deionized water to prepare a solution containing Fe and Ni at the desired molar contents of 0.011 mol Fe and 0.011 mol Ni. The obtained solution was mixed with a kind of sodium fatty acid (0.055 mol), ethanol (40 mL) and n-hexane (70 mL) in a three-neck round flask, and then reacted at 70 °C for 5 h under stirring [16]. After reaction, the products were divided into two layers. The upper organic layer was obtained through a separating funnel, which was washed three times using deionized water, and then dried at 110 °C for 3 h in a bake oven to obtain the oil-soluble iron-nickel bimetallic catalyst precursor.

Molybdenum naphthenate catalyst with the molybdenum content of 6.07 wt% was prepared according to the literature [17] as a contrastive oil-soluble Mo catalyst for coal/oil co-processing.

2.3. Sulfurization of catalyst precursor

1000 μg·g^{-1} of synthesis catalyst precursor (based on metal content, the same below), 0.5 g elemental sulfur and 150 g wax oil were mixed and subsequently subjected to an autoclave. The sulfidation reaction was carried out at 360 °C for 1 h under an initial hydrogen pressure of 8 MPa. The solid product was centrifugally washed with enough toluene and ethanol, and then stripped and dried under nitrogen atmosphere to obtain the sulfurized catalyst.

2.4. Characterization of catalyst

The oil-soluble properties of the catalyst precursor were investigated by mixing with water, mineral ether, toluene and kerosene according to the volume ratio of 1:20 [18]. The specific surface area (SSA) of sulfurized catalyst was about 26.6 m^2/g, based on the BET method (TriStar II 3020, Micromeritics Instrument Corporation). The Fourier transform infrared (FTIR) spectra were recorded with a FTIR spectrometer (Thermo Nicolet) to determinate functional groups of the catalyst precursor. The thermal stability of the catalyst was investigated with STA6000 analyzer. In STA6000 thermogravimetric (TG) analyzer, the catalyst precursor was heated from 30 °C to 800 °C at 10 °C/min under a 40 mL/min N$_2$ gas flow to investigate the thermal stability. The crystalline structure of the sulfurized catalyst precursor was investigated by X-ray diffraction (XRD, Rigaku D/Max-III C, Netherlands) using Cu Kα radiation. The software of X' pert Fighscore plus was used for the phase analysis of sulfurized catalyst based on the standard card of XRD-PDF-2004. Transmission electron microscopy (TEM) images of the sulfurized catalyst precursor was obtained by JEOL JEM-2100UHR microscope. The diameter distribution of sulfurized catalyst precursor was determined by a Laser particle sizer (MasterSizer2000).

2.5. Coal/oil co-processing reactions

The catalytic performance of the synthesized catalyst precursor was studied in a 500 mL stirred autoclave. The same reaction processes were