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Research article

Hydrocracking of low-temperature coal tar over NiMo/Beta-KIT-6 catalyst to produce gasoline oil

Jipeng Meng, Zhiyong Wang, Yanhong Ma, Jiangyin Lu *

Key Laboratory of Oil & Gas Fine Chemicals, Ministry of Education, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, China

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ABSTRACT

In current study, NiMo catalysts supported on micro-mesoporous composite material Beta-KIT-6 were prepared and characterized by SEM, TEM, XRD, BET and NH_3-TPD. This micro-mesoporous composite catalyst was employed in hydrocracking of low-temperature coal tar (LTCT) for the first time on a fixed-bed reactor. The effects of temperature, pressure, weight hourly space velocity and hydrogen/oil ratio on hydrocracking performance were examined. The research octane number (RON) value and paraffins (P), olefins (O), naphthenes (N) and aromatics (A), i.e. PONA content of gasoline fraction was determined. The yield of light oil (≤300 °C) can reach 95% including gasoline fraction (≤180 °C) accounting for 88% and diesel fraction (180–300 °C) for 7%. Sulfur and nitrogen contents were significantly reduced from 0.67 and 1.79 wt% in the feed to below 50 and 20 mg kg^{-1} in the gasoline, respectively. Besides, the RON value of gasoline can reach 79. The results indicated that raw LTCT could be considerably upgraded by catalytic hydrocracking over the prepared catalyst, which may offer a route for further processing and application of LTCT.

1. Introduction

In order to cope with petroleum depletion crisis and ensure global energy security, developing various substitute energy sources, such as coal-derived liquid, oil shale crude, tar sands, has become an important and urgent task [1–3]. In China, coal is the chief energy resource and extensive studies have been focused on coal-to-liquids (CTL) technology [4], which results in over 10 million tons of byproduct, i.e. coal tar, from coal gasification and carbonization during the pyrolysis every year [5]. Currently, except for only tiny amounts of coal tar used to produce chemical products, most is used directly as an energy fuel for combustion, leading to significant resource waste and environmental contamination. Therefore, coal tar hydrogenation, which cannot only make full use of coal tar but also relieve the growing crisis in energy, has received substantial attention as one of the most attractive alternatives for producing lighter and more valuable clean fuel, such as gasoline, kerosene and diesel. Generally, coal tar, a complex dark brown or black mixture consisted of aliphatic, alicyclic, aromatic, and heterocyclic compounds [6], can be divided into HTCT (high-temperature coal tar, 1000 °C), MTCT (middle-temperature coal tar, 800 °C) and LTCT (low-temperature coal tar, 650 °C) based on the pyrolysis temperature [7]. However, high contents of sulfur, nitrogen, oxygen and trace amounts of metals in coal tar severely affects the catalytic stability and activity of hydrocracking. Therefore, stable and highly active catalysts for coal tar hydrogenation to light oil are vital to the hydrogenation process.

The complexity of coal tar has driven researchers to mainly focus on the hydrogenation of a pure model compound such as naphthalene [8,9], phenanthrene [10], thiophene [11], dibenzothiophene [12,13] and quinolone [14], rather than on a real fraction. Extensive investigations about hydrocracking performance of model compounds over hydrogenation catalysts loaded on various supports were performed. The activity of hydrogenation catalysts is highly dependent on the physicochemical properties of the support [15,16]. At present, extensive researches on model compounds hydrogenation catalyst supports are focused on mesoporous materials such as MCM-41 [17], HMS [18], and SBA-15 [19]. The catalysts supported on these materials showed high hydrogenation activity and poison resistance, but the wide application of these materials in industry is limited due to their bad mechanical properties and poor thermal stability [20,21]. For catalytic cracking process of real coal tar, γ-Al_2O_3 [22–24] is a common support which can load amounts of metals, such as NiMo, MoCo and NiW. Besides, USY [25,26] zeolite catalyst has been found to show high hydrogenation and cracking activity and to effectively improve the yield of light oil. Promising coal tar hydrocracking results including high-quality oil products along with high sulfur and nitrogen removals were achieved. However, it has been found that the oil yield only account for about 20% of the products. Besides, it need to be performed under a severe condition with pressure about 10–16 MPa and high hydrogen/oil ratio (1400–1800), leading to a high cost and hydrogen consumption.

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* Corresponding author.
E-mail address: jiangyinlu6410@163.com (J. Lu).

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Recently, novel composite materials [27–31] with appropriate physicochemical properties such as large surface area, tunable pore size, good thermal and mechanical resistance were employed as supports for hydrogenation process extensively. For instance, Zhang et al. [32, 33] prepared the micro–mesoporous composite materials Beta-KIT-6 and Beta-SBA-15 from zeolite Beta seeds by two-step hydrothermal crystallization method, with good results in the dibenzothiophene hydrodesulfurization process. Beta-MCM-41 was also used as a composite support to prepare a supported NiW HDS catalyst [34], and the catalyst showed higher catalytic activity than a pure Al_2O_3-supported catalyst. The acidic supports could promote the catalytic cracking activity and accelerate the hydrocracking process, and 3D mesoporous materials with large pores could weaken the diffusion resistance and enhance mass transfer. Beta-KIT-6 supported catalysts can effectively integrate the superior acidity properties of Beta and the cubic Ia3d mesoporous structure of KIT-6, which can exhibit higher hydrocracking catalytic activity than the pure Beta and KIT-6 supported ones. Moreover, compared with Beta-MCM-41 and Beta-SBA-15, micro-mesoporous material Beta-KIT-6 possesses the large pore (about 7 nm) cubic Ia3d mesostructure which can further enhance the accessibility of the active sites to reactant molecules [32]. This superior mass transfer property combined with the appropriate acidity makes Beta-KIT-6 more suitable for hydrocracking of heavy oil which contain high contents of sulfur and nitrogen.

Based on what have been discussed above, although extensive investigations devoted to the hydrogenation of model compounds, few dealt with the hydrocracking of LTCT over catalysts supported on micro-mesoporous composite material. In present study, we prepared the Beta-KIT-6 material by two-step hydrothermal crystallization method firstly. Then the Beta-KIT-6 support and the supported NiMo catalysts were obtained and characterized by various techniques. And then the hydrocracking of LTCT over NiMo catalysts was carried out in a continuous fixed bed reactor under various reaction variables, including reaction temperature, reaction pressure, weight hourly space velocity (WHSV) and hydrogen to LTCT volume ratio (hydrogen/oil ratio). Then the gasoline and diesel fractions distilled from the oil product were analyzed. The results provide basic knowledge about micro-mesoporous composite material for the first time in hydrocracking of the LTCT. And the gasoline oil product may serve as a promising blending compound for producing low sulfur and nitrogen contents gasoline.

2. Experimental

2.1. Catalysts preparation and ex-situ presulfidation

The Beta-KIT-6 (designated as BK) material was prepared by following the published procedure [32]. NiMo/BK catalysts were prepared by incipient wetness impregnation method using BK material as support and appropriate amount of ammonium heptamolybdate and nickel nitrate. Weighing amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$, fully dissolving them by distilled water in two separate beaker, then a certain concentration of the solution was achieved. Pouring the two solutions into a rotary evaporation flask to form a uniform solution, then the prepared BK composite molecular sieve was poured into the flask. Kept the rotary evaporator in a water bath stirring at 40 °C for 12 h, then dried at 80 °C in vacuum and dried under 90 °C for 6 h by blowing, and calcined at 500 °C for 5 h. Then the NiMo/BK catalysts with different Mo loading (8, 10, 12, and 14 wt% of MoO_3) and the unchanged loading of Ni (NiO 4 wt%) were obtained.

And then, the catalyst presulfiding was conducted. The catalytic activity of presulfided catalyst can be improved by changing the form of active sites from metal oxide to metal sulfide. Usually, the catalyst presulfiding process is carried out using either the in-situ or ex-situ technology. In-situ presulfidation is a relatively difficult and time-consuming procedure. Compared to the in-situ method, a more elegant way which utilized ex-situ presulfided catalyst can accelerate the start-up of the hydrocracking process, since the catalyst can be activated in-situ at a relatively mild temperature under hydrogen during start-up [35,36]. Therefore, in this work, the ex-situ presulfided catalyst was obtained by incipient wetness impregnation of the NiMo/BK in oxidation state with a certain concentration of $(NH_4)_2S_2O_3$ solution in a rotary evaporator. The molar ratios of S/Mo and S/Ni were 3 and 1, respectively. After impregnated for 12 h at 40 °C and dried for 6 h at 50 °C in vacuum, we extruded it into a columnar catalyst of $\Phi\, 3\times 5$ mm, dried at 50 °C for 12 h in vacuum to achieve the final presulfided catalyst.

2.2. Catalysts characterization

Scanning electron microscopy (SEM, S-4300) was performed with an acceleration voltage of 30 kV at a high operating mode of the vacuum. High-resolution transmission electron microscopy (TEM, Tecnai G2 F20), which operated at an acceleration voltage of 200 kV, was also utilized to investigate the structure of the catalyst. X-ray diffraction (XRD) was performed using the M18XHF22-SRA X-ray diffraction instrument of Japanese Mac Scienc company using Cu Kα as the radiation at 35 kV and 25 mA and scanning in the range of 5–70 °C with a scanning-rate of 2 °C min^{-1}. The crystal structure, physical phase and dispersion of the catalyst were mainly analyzed. The Brunauer-Emmett-Teller (BET) specific surface area, pore volume, and average pore diameter were obtained via nitrogen gas absorption and desorption isotherm method by Builder ASAP2020 absorber (Micromeritics Builder Tech., Ltd.). The sample was degassed purification at 300 °C for 4 h under vacuum at a pressure of 15 μm Hg, then analyzed by static adsorption method under N_2 atmosphere at −196 °C. Temperature-programmed desorption of NH_3 (NH_3-TPD) was carried out using TP-5080 Automatic Dynamic Analysis of adsorption instrument manufactured by Tianjin Xianquan Instrument Co. Ltd. 0.1 g test sample placed in the quartz glass sample tube, then heated to 400 °C in 1 h according to the program with the rate of 30 ml min^{-1} of the helium gas. The experiment on NH_3 saturation adsorption has been conducted in 30 min with a rate of 10 ml min^{-1} of NH_3 (about 0.1 MPa) after cooled to room temperature. Then the sample was heated to 120 °C and the rate of helium was 40 ml min^{-1}. Finally, warmed up to 600 °C according to the program with the rate of 10 °C min^{-1}, export desorption curve the NH_3-TPD spectrogram can be obtained, and it was used to analyze the tendency of the acidity and acid amount of the catalyst.

2.3. Analysis methods of raw feed and products

The LTCT obtained from Xinjiang province was used to investigate the hydrocracking performance of the catalyst. Table 1 shows its main

Table 1
Properties of the LTCT.

Properties	Value
Density, (g cm^{-3})	0.95
Elemental analysis (wt%)	
C	84.97
H	11.53
S	0.67
N	1.79
O*	1.04
H/C molar ratio	1.63
Distillation range, °C	
IBP	199
10%	265
30%	293
50%	351
90%	467
FBP	504

*: the oxygen content was calculated by the subtraction method.