



Short communication

Acid treated halloysite clay nanotubes as catalyst supports for fuel production by catalytic hydrocracking of heavy crude oil



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HIGHLIGHTS

- Heavy oil residue was catalytically hydrocracked to obtain liquid fuels.
- NiO and CoO were seeded on acid leached halloysite nanotubes and used as a suspended catalyst.
- Proposed method allowed to obtain fuels at significantly lower hydrogen gas pressure of 1 MPa.
- Total yield of the gasoline and diesel varied at 52–57% range.
- Obtained diesel and gasoline can be used as motor fuels after further desulfurization treatment.

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ABSTRACT

Acid treated halloysite nanotubes were utilized as a support for the NiO and CoO catalysts for the hydrocracking of the heavy oil residua obtained from vacuum distillation of the Azerbaijan crude oils. Halloysite was treated with hydrochloric acid prior to seeding the catalysts. Catalysts were further activated in plasma furnace at 850 °C under argon atmosphere. Oil residue was hydrocracked with the catalyst at 450 °C and 1–4 MPa pressure range. Increase of the hydrogen gas pressure from 1 to 4 MPa caused increasing the yield of the liquid fuels (gasoline and diesel) from 52% to 57%. Compositions of the gasoline and diesel fractions were analyzed in detail and it has been established that these products can be used as a fuel in vehicles with further desulfurization process.

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1. Introduction

Catalytic hydrocracking of heavy crude oil leftover from petroleum refining is one of the most effective ways to increase the yield of the fuel production in modern refineries. Currently, heavy residua left from crude oil processing constitute roughly 30–40% of the feed in average petrochemical refinery [1]. Hence there is a tremendous potential for fuel production by increasing the depth of the crude oil cracking.

Thermal and catalytic cracking of residual heavy oil has very low yields for light fuels and requires high quality feedstock (high H/C ratio and low metal content), which makes this process less likely than hydroprocessing. On the other hand, typical hydrocracking process requires high pressure (10–20 MPa) and consumes

substantial amount of hydrogen, which is not economical [2,3]. Presence of high molecular asphaltene in the petroleum residua offers another challenge for the catalytic processes as they cannot easily penetrate into fine pores of the catalysts, which reduces the efficiency of the hydrocracking [4]. In addition these molecules quickly dehydrogenate and deposit on the outer surface of the catalyst by deactivating it [2]. This necessitates the use of mesoporous catalysts for hydrocracking of heavy crude oil residues [5].

Halloysite nanotubes are naturally occurring clay minerals with tubular structures of submicron size and inner lumen diameters ranging from 10 to 50 nm depending on natural deposits, which is significantly larger than the pores of zeolites [6,7]. Halloysite mined from Dragon mine in Utah was utilized as a petroleum cracking catalyst before the introduction of synthetic zeolites [8]. Nowadays, halloysite is mainly studied as additives for polymers and for controlled release applications [9–11]. Recently, halloysite nanotubes along with zeolite catalysts were shown to be very

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efficient in increasing the gasoline yield and lowering the coke formation during catalytic cracking of the vacuum gasoil and cottonseed oil mixtures [12,13] due to deeper cracking of the large molecular weight species. In this work we attempted to analyze the halloysite nanotubes decorated with nickel and cobalt oxide catalysts for the catalytic hydrocracking of heavy crude oil obtained from petroleum of Azerbaijan republic with the purpose of deepening the oil-refining process and increasing the yield of the gasoline and diesel fractions. Another purpose of this work is to demonstrate the possibility of low pressure hydrocracking of residual heavy oil using this catalyst.

2. Materials and methods

2.1. Materials

Halloysite nanotubes were obtained from Petkim Petrokimya Holding (Turkey). Hydrochloric acid solution (36%), cobalt (II) chloride and nickel (II) chloride (chemical grade, 98.5% purity) were obtained from Ural plant of chemicals (former Ural plant of chemical reagents, Russian Federation) and used as received. Heavy crude oil residua (5% boils at 450 °C, 30% boils at 500 °C) were obtained by vacuum distillation of the Azerbaijan crude oils and received from Heydar Aliyev Petrochemical Refinery (Azerbaijan). Further properties and composition of the heavy oil are presented in Table 1. Ultrahigh purity hydrogen gas (99.999% purity) was obtained from Sharjah Oxygen Company (United Arab Emirates).

2.2. Methods

Halloysite was characterized by Transmission Electron Microscope (Zeiss EM 912). Elemental compositions of the catalysts were determined by X-ray Analytical Microscope (XGT-7000, Horiba, Japan). FT-IR-spectra of the catalysts were recorded with “Bruker ALPHA FT-IR” spectrometer in the range of 400–4000 cm^{-1} . Compositions of hydrocracking products were analyzed using gas chromatography (Autosystem XL, Perkin Elmer) and NMR (Bruker, 300 MHz) spectrometers. Chromatographic separations were achieved using helium gas in Zebtron ZB-1 capillary column coated with dimethyl polysiloxane polymer as stationary phase. Octane numbers were calculated based on compositions of the gasoline fractions obtained from gas chromatograph (Autosystem XL, Perkin Elmer). Sulfur content in gasoline and diesel fractions was determined with SLFA-20 X-ray fluorescence sulfur-in-oil analyzer (Horiba Scientific) by ASTM D-4294 method. Freezing point was determined with Seta Freezing Point Apparatus (Stanhope-Seta Ltd.) by ASTM D2386 method. Flash point was determined with Cleveland Flash Point Testing Equipment (Stanhope-Seta Ltd.) according to ASTM D92 standard. Densities of the gasoline and diesel fractions were measured with density meters (DMA 4500 M, Anton Paar) by ASTM D5002 method. Kinematic viscosity and composition of the heavy oil were determined by ASTM D445, ASTM D2887 and ASTM D7169-11 standard methods. Distillation fractions were determined with crude oil distillation system (BR Instruments Company, USA) by ASTM D2892 standard. Iodine number was determined by reacting sample with iodine in chloroform solution and titrating the residual iodine with sodium thiosulfate as described in [13].

2.3. Preparation of the hydrocracking halloysite catalysts

Halloysite (about 100 g) was dried at 200 °C for 2 h. Then it was treated with 100 mL of 2.5N HCl solution for removing contaminants from the surface and inner halloysite pores. Halloysite is mixed with HCl solution in 1:10 mol ratio for 6 h until a homoge-

neous mixture is obtained. Once the processes ended halloysite was separated from the suspension by centrifuge and washed with water until no chloride ion was detected in the sample and dried at 100 °C. This has been labeled as H-halloysite. H-halloysite was mixed with aqueous solution of metal chloride in 1:10 mol ratio (halloysite: metal chloride) at 90 °C for 6 h, then dried at 100 °C. The dried sample was processed in CVD plasma furnace (NaBond Technologies Co., China) under argon atmosphere at 850 °C for 4 h.

2.4. Hydrocracking of the heavy crude oil

Hydrocracking of heavy crude oil was carried out in a 250 mL tube microreactor. About 300 g of crude with dispersed catalyst (2.5% by weight) was measured with burette and pumped to the reactor with 250 mL/h feed rate, where it is mixed with H_2 from cylinder. Pressure of the hydrogen gas was varied from 1 to 4 MPa. The reactor is made of stainless steel, and set in a block of aluminum bronze, which provides uniform temperature distribution across its volume during the overall process. Temperature in the reactor is measured by thermocouples and regulated by electronic potentiometer to be 450 °C. The reaction products and left-over hydrogen gas proceed to the shell-and-coil condenser from the top of the reactor and then further to the ice-cooled separator-receiver in which separation of liquid hydrocarbons from gaseous products of reaction and hydrogen takes place. Liquid products together with suspended catalyst are collected from the bottom clock of the receiver and filtered from the catalyst and other suspended solids formed during the reaction (coke). Ash-free liquid products are distilled to separate gasoline (b.p. >200 °C) and diesel fractions (b.p. 200–360 °C). A residue with boiling point above 360 °C is a viscous liquid. Gaseous products passed through gas clock for measuring their volume, and exhausted into atmosphere. The rate of gas flow was regulated by the valve on the outlet of the separator.

3. Results and discussion

3.1. Halloysite

Halloysite with the idealized chemical formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ is similar to kaolinite except for the presence of water between the adjacent layers of clay. This water is easily lost upon heating and such halloysite was used in current study.

Unlike kaolinite halloysite has tubular morphology with hollow inner pores extending along its length. Tubes are formed by multi-layer roll of sheets having SiO_4 tetrahedrons and AlO_6 octahedrons. External surface of the tubes is comprised of silica while inner pore surfaces are made of the alumina. Dimensions of the tubes vary at 0.5–2.0 μm range in length, and 50–100 nm range in diameter. Inner pore diameter is at 10–20 nm range. Smaller pores (>3 nm) mainly originate from defects at halloysite tube endings and spaces between rolled layers (Fig. 1A and B).

Original and acid treated H-halloysite was analyzed with thermo-gravimetric analyzer to assess thermal stability under reaction conditions. The investigations are conducted at temperature of 20–900 °C in nitrogen atmosphere by ramping the temperature at 10 °C/min rate. Halloysite loses about 12% of its weight at 500 °C due to degradation of Al-OH octahedral sheets into Al_2O_3 and hence converts into metakaolin, though tubular morphology is preserved up to 900 °C. Acid treated H-halloysite does not show any weight loss apart from 1% initial surface moisture at 100 °C, indicating effective removal of aluminum oxide layer (Fig. 1C).

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