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Hematite nanoparticles in aquathermolysis: A desulfurization study of thiophene

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HIGHLIGHTS

- Hematite nanoparticles displayed good performance in decomposing thiophene.
- The catalytic performance increases with temperature and catalyst concentration.
- The use of hydrogen donor could reduce the catalytic activity.
- A cyclic phase transformation of hematite to magnetite was observed.

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ABSTRACT

The potential usage of hematite nanoparticles as heterogeneous catalysts in aquathermolysis was investigated in this work. The desulfurization of thiophene was studied to investigate the catalytic activity of hematite in the aquathermolysis of heavy oil. It was found that reaction conditions, e.g., reaction time and temperature, ratio between thiophene and water, hematite nanoparticle size, catalyst concentration, and the presence of hydrogen donors, influenced the ability of hematite nanoparticles to decompose thiophene. Experimental results showed that thiophene conversion was increased with reaction time, temperature and catalyst concentration but decreased with thiophene/water ratio and particle size. Further analysis showed that the activity of the hematite nanocatalyst was also reduced in the presence of hydrogen donors. This is because hydrogen donors occupy the catalyst surface and block the catalytic sites. Furthermore, FTIR and XRD analyses revealed that thiophene underwent oxidative desulfurization to produce maleic acid, SO_2 and CO_2, whereas some areas of the hematite surface were transformed into magnetite. However, this magnetite was re-oxidized back into hematite in the presence of water as the source of active oxygen.

1. Introduction

Heavy oil, a major component of total unconventional oil reserves, has become a major research focus in the past decades because of the depletion of conventional light oil resources. However, the exploration and production of heavy oils present special challenges compared to conventional light oil, due to their physical and chemical properties. Heavy oil has very high viscosity and is composed of a high amount of heteroatomic components such as resins and asphaltene, which pose the main challenges to its production, transportation and processing [1]. In the past several years, many new technologies related to the optimization of heavy oil production have been reported, such as thermal, chemical, and biochemical recovery [2–11]. Comparison studies of these methods suggest that thermal recovery via catalytic aquathermolysis is by far considered as the most effective method to extract heavy oil [11]. In general, catalytic aquathermolysis refers to a process where steam and a catalyst (sometimes with hydrogen donors) are injected into the reservoir rock in order to maximize heavy oil production by reducing its viscosity. The reduction of the oil viscosity during this process is mainly due to the degradation of the large hydrocarbon molecules such as asphaltene and resin in the heavy oil [11–14]. Hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemethylation, hydrocracking, and hydrogenation have been reported during the aquathermolysis process [15–17].

In catalytic aquathermolysis, different types of catalysts, such as iron-based catalysts, have been widely reported [11]. Various type of iron-based catalysts, such as $FeSO_4$, Fe-naphthenate,

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$Fe(CH_3COCHCOCH_3)_3$, iron (III) dodecylbenzene sulfonate, and iron-based ionic liquid, have been successfully used in aquathermolysis [1,18–21]. The mechanism of these iron-based catalysts to catalyze aquathermolysis reaction has always been associated with Fe (II)/Fe (III)'s ability to form a strong interaction with hydrocarbon molecules in heavy oil. For example, Rosales reported that strong Fe-asphaltene interactions were formed in the presence of water and electron–donor additives [22]. Based on the calculation, these interactions occurred between Fe and aromatics rings or Fe and heteroatoms (N or S) in asphaltene molecules. As a result, these interactions would decrease bond energies (bond activations) of C—C, C—N, and C—S bonds in asphaltene molecules, giving rise to the activation of these bonds for cracking, HDS and HDN reactions [22].

It is widely known that hematite (α-Fe_2O_3) is one of the most naturally abundant type of iron oxide mineral phases [23]. Due to its unique physical and chemical properties, hematite has many advantages such as nontoxicity, abundance, inexpensiveness and stability, and hence has been studied in wide variety of applications [24–31]. For oil and gas applications, recent studies have shown that hematite can be used as a highly active heterogeneous catalyst in the catalytic steam hydrocracking of petroleum residual oil [32–34]. In this paper, the application of hematite nanoparticles as catalyst in aquathermolysis was studied. Hematite nanoparticles were synthesized using a simple and facile hydrothermal method according to our previous work [35]. The effects of reaction time and temperature, amount of catalyst, ratio of thiophene/water, size of hematite nanoparticles, and the presence of a hydrogen donor were investigated in terms of thiophene conversion. Moreover, the possible catalytic mechanism of thiophene on the hematite nanoparticle surface was also investigated in this study.

2. Experimental methods

2.1. Materials

For the synthesis of hematite nanoparticles, iron (III) chloride hexahydrate was purchased from Alfa Aesar® and used as the iron source. Ammonium hydroxide and ethanol were purchased from Sigma–Aldrich®. For the aquathermolysis reaction, thiophene and hexane were purchased from Sigma–Aldrich® and used as a representative oil feedstock and solvent, respectively. While 1,2,3,4-tetrahydronaphthalene (tetralin) from Acros Organics® was used as the hydrogen donor.

2.2. Preparation of hematite nanocatalyst

Hematite nanocatalysts were synthesized via hydrothermal method according to our previous work [35]. In this method, a mixture of aqueous iron (III) chloride and ammonium hydroxide solution was prepared and heated at 120 °C for 24 h in a Teflon-lined stainless-steel autoclave. The reaction products were then centrifuged and washed with distilled water and ethanol three times, and finally dried under vacuum at 70 °C for 12 h. The hydrodynamic particle size of the hematite nanoparticles was determined by Microtrac Zetatrac (Model NPA152-31A), a dynamic light scattering (DLS) analyzer.

2.3. Characterization

For the characterization of hematite nanocatalyst before and after aquathermolysis reaction, FTIR and XRD analysis were performed. The FTIR spectra of samples were obtained using with a Thermo Scientific Nicolet Avatar 370 DTGS FTIR Spectrometer. An X-ray diffraction study of the nanoparticles was carried out using a PANalytical X'Pert Pro diffractometer equipped with PIXcel detector (PANalytical B.V., Almelo, Netherlands). The measurements were performed on zero-background silicon plates with the diffraction angle from 6° to 70° using Cu Kα radiation. Data were collected using X'Pert Data Collector software and processed using X'Pert HighScore Plus (PANalytical B.V.). The BET surface areas of the synthesized hematite nanoparticles were measured using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The BET-specific surface area of the nanoparticles measured was 25.05 m^2/g.

2.4. Catalytic desulfurization of thiophene

To investigate the catalytic performance of hematite nanoparticles in aquathermolysis, thiphene was desulfurized in a Teflon-lined autoclave-like reactor (~100 ml in volume) fabricated in our laboratories. As the feedstock, thiophene in hexane solution with known initial concentration was mixed with water (ratio 7:3) and used as the feedstock. Furthermore, 10% v. of hydrogen donor (tetralin) was added into the mixture along with hematite nanoparticles as the catalyst. The mixture was then heated up to different series of reaction temperature, i.e., 120–180 °C and reaction times, i.e., 12–72 h. After the reaction, the reactor was cooled naturally to room temperature. The catalytic performance of the hematite nanocatalyst was determined by the conversion of thiophene after the reaction. An Agilent 7890A Gas Chromatograph equipped with an Agilent J&W HP-5 Column was used to measure thiophene concentration after the reaction. In addition, a similar reaction procedure was carried out to study the effect of water in the reaction by changing the ratio of thiophene and water to 7:3, 1:1, and 3:7. Moreover, two other reactions, i.e., with hydrogen gas (100 psi) as the hydrogen donor and in the absence of hydrogen donors, were conducted to study the effect of hydrogen donors in the desulfurization of thiophene.

3. Results and discussion

3.1. Catalytic activity of hematite nanocatalyst

In order to study its potential application for catalysis of heavy oil in aquathermolysis, the catalytic performance of hematite nanoparticles in thiophene desulfurization was investigated. Fig. 1a presents thiophene conversion at various temperatures during 12–72 h of desulfurization reaction. The results clearly indicated that thiophene started decomposing even at a relatively low temperature (120 °C) on the hematite nanocatalyst surfaces. Results also showed that thiophene decomposition increased with time up to 24 h. After that, no significant increment of conversion was observed when the reaction time was further increased to 48 and 72 h. A review of the literature shows that different type of catalysts have been used in desulfurization; for example, some transition metals or binary metals and their sulfides, either supported or non-supported [36–40]. However, these catalysts require high reaction temperature (>300 °C) in order to ensure the effectiveness of thiophene decomposition. For example, a study by Wang and Iglesia reported that a supported Ru cluster catalyst was successfully used for desulfurization of thiophene in the presence of hydrogen gas [39]. Based on their report, it was found that SiO_2 supported Ru metal cluster catalysts were able to effectively and selectively catalyze both the desulfurization and hydrogenation of thiophene (reaction time: 15 h; catalyst concentration: 0.3 wt.%, temperature: 623 K; and 3 MPa of H_2). In another study, it was reported that an alumina supported bimetals catalyst of Ni—Mo could convert about 55% of thiophene in a fixed bed reactor containing 200 mg of catalyst at reaction temperature of 450 °C