Hematite Nanoparticles in Aquathermolysis: A Desulfurization Study of Thiophene

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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, SO₂ and CO₂, 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.

Keywords

Aquathermolysis, hematite, desulfurization, heterogeneous catalyst

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 FeSO₄, Fe-naphthenate, Fe(CH₃COCHCOCH₃)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 -Fe₂O₃) 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 hours 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 hours. 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 K α 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 m²/g.

2.4. Catalytic Desulfurization of Thiophene

To investigate the catalytic performance of hematite nanoparticles in aquathermolysis, thiophene 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°C–180°C and reaction times, i.e., 12–72 hours. 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. Figure 1a presents thiophene conversion at various temperatures during 12–72 hours 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 hours. After that, no significant increment of conversion was observed when the reaction time was further increased to 48 and 72 hours. 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 SiO₂ supported Ru metal cluster catalysts were able to effectively and selectively catalyze both the desulfurization and hydrogenation of thiophene (reaction time: 15 hours; catalyst concentration: 0.3% wt., temperature: 623K; and 3 MPa of H₂). 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 with 20 ml/min flow rate of hydrogen for 8 hours.⁴⁰ In this work using hematite nanoparticles as a catalyst, our results show that ~23% conversion of thiophene has already been achieved at 120°C. Furthermore, an improvement on the catalytic performance was observed when the reaction was carried out at higher temperatures (Fig. 1a). Based on the results, 34% of thiophene conversion was achieved when the reaction was carried out at 180°C for 72 hours.

The effect of hematite nanoparticle concentration on hematite's ability to convert thiophene by desulfurization is presented in Fig. 1b. The results clearly display that the conversion of thiophene was significantly affected by the amount of hematite nanocatalyst present in the sample. Results also showed that no conversion of thiophene was observed in the absence of hematite nanoparticles at the reaction temperature of 150°C. This non-reactivity was due to the stability of thiophene, as it is an aromatic compound and fairly stable towards hydro-decomposition. A similar result was also observed in another group of sulfur-containing compounds, a hydrodesulfurization study of 4,6-dimethylbenzothiophene over alumina-supported Pt, Pd, and Pt-Pd catalyst.³⁶ However, our results indicate that thiophene started decomposing when even a very small amount of hematite nanoparticles (0.0275% wt.) was added. This result suggests that the reactivity of thiophene towards desulfurization was greatly improved in the presence of hematite nanoparticles, which are essentially acting as a catalyst. It is believed that the improvement of this reactivity is due to the activation of the C-S bond in thiophene as thiophene interacts with the hematite surface.^{22,41} As expected, further decomposition of thiophene was observed when the amount of catalyst was further increased to 0.05% wt. (Fig. 1b). This is true since more catalytically active surfaces could be provided as more catalysts were added into the reaction. Thiophene conversion was further improved to

22.4% when 0.075% wt. of hematite nanoparticles was used. Finally, when 0.1% wt. of hematite nanoparticles were added, as high as 26.3% of thiophene conversion could be achieved. In addition, the results also demonstrated that the effect of concentration on the catalytic activity of hematite nanoparticles was slightly less significant at concentrations of catalyst beyond 0.05% wt. This phenomenon could be the result of particle aggregation at high concentrations, which ultimately reduces the availability of catalytically active surface for the catalysis. Therefore, adding more catalysts than 0.05% wt. would only slightly increase the ability of hematite nanoparticles to convert thiophene by desulfurization.

The effect of thiophene/water ratio and hematite nanoparticle size on the catalytic performance of hematite nanoparticles in desulfurization reaction was also investigated. Figure 2 presents the desulfurization activity of hematite at different thiophene/water ratios and hematite nanoparticle sizes. Figure 2a indicates that the amount of water present during the reaction had a significant influence on the reactivity of thiophene towards desulfurization. The results clearly show that the amount of thiophene conversion was gradually improved when more water was introduced into the reaction system. In the reaction where thiophene was more dominant than water, for example, thiophene/water ratio = 7:3, the conversion of thiophene was less effective. Greater thiophene conversion was obtained when the thiophene/water ratio was 3:7. A similar effect of water on the catalytic activity of hematite was also reported by Fumoto and co-workers in their study on the catalytic steam cracking of heavy oil.³² It was believed that the crystalline phase of the hematite surface was changed during the conversion of heavy oil to its light fraction. Lattice oxygen in the hematite surface oxidized heavy oil to produce light oil and CO₂.³² As a result of this oxidation, part of the hematite surface was reduced to magnetite. However, in the presence of water steam, oxygen from water was supplied to the catalyst to reconstruct hematite

back from magnetite. Therefore, hematite structure was maintained during the reaction when enough oxygen species from water was provided. As a result, when more water was introduced into the desulfurization, more oxygen could be generated from the water and better thiophene desulfurization could be achieved. Figure 2b presents the effect of hematite nanoparticle size on the desulfurization of thiophene, showing that the activity of the catalyst was reduced by the increments of catalyst particle size because the availability of surface area for catalytic reaction is higher when catalyst size is reduced to nanoscale.

3.2. Role of Hydrogen Donor

In many aquathermolysis studies, several types of hydrogen donors such as tetralin, cyclohexane, methylcyclohexane, and formic acid have been proven to improve heavy oil degradation by donating active hydrogen to the reaction.¹¹ The effect of the hydrogen donor on hematite nanoparticle performance for thiophene conversion was investigated in this research. Figure 3 shows the catalytic activity of hematite nanoparticles in the presence and absence of tetralin and hydrogen gas as hydrogen donors. It was observed that the presence of a hydrogen donor, both the tetralin and hydrogen gas, reduced the catalytic activity of hematite nanoparticles to decompose thiophene. For example, when the reaction was carried out without a hydrogen donor, 47% of thiophene was converted into other products. Conversely, when the reactions were performed in the presence of tetralin or hydrogen gas, the conversions were at about 37% and 42.4%, respectively (Fig. 3). It is believed that the overall desulfurization reaction involves initial adsorption of thiophene onto the catalyst surface, which activates the molecule and is followed by C-S bond scission to get the final products.⁴² The presence of a hydrogen donor can transfer hydrogen to the reactant and improve the catalyst activity. However, our results

indicated that the presence of a hydrogen donor decreased the catalytic activity. After carefully examining the products with GC as tetralin was used as the hydrogen donor, it was observed that the amount of tetralin remained the same before and after the reaction. Moreover, tetralin was expected to convert into naphthalene with 1,2-dihydronaphthalene as intermediate if hydrogen was transferred from tetralin to thiophene.⁴³ However, analysis of the reaction products indicated no sign of naphthalene or 1,2-dihydronaphthalene was obtained. This suggested that tetralin remained unreactive during desulfurization when hematite nanoparticles were used as catalyst. Therefore, it is possible that the C-S bond scission dominates the reaction of thiophene decomposition on the hematite nanoparticle surface. When tetralin was introduced as the hydrogen donor, the adsorption of tetralin onto the catalytic surface occupied the surface area and hence decreased the possible adsorption of thiophene, resulting in the reduction of catalytic activity.

Figure 3 also show a significant increment of thiophene conversion when hydrogen gas was used as the hydrogen donor instead of tetralin (Fig. 3). This phenomenon can be explained by taking into account the surface availability of hematite for the reaction due to adsorption of tetralin and hydrogen. When hydrogen gas was used as the hydrogen donor, more hematite surface was available for desulfurization because the size of the hydrogen molecule is significantly smaller than the size of tetralin. In addition, it is also possible that the presence of hydrogen gas can reduce some hematite to magnetite. Therefore, the reduction of catalytic activity of hematite, comparing with no hydrogen donor, could be the result of both catalytic surface occupation and catalyst reduction in the presence of hydrogen gas.

3.3. Catalytic Mechanism

In order to investigate the catalytic mechanism of thiophene decomposition with hematite nanoparticles, the particles were collected before and after the reaction for further analysis using FTIR. Figure 4 presents the FTIR spectra of hematite nanoparticles before and after reaction. The IR spectra in Fig. 4a displayed only two sharp peaks at 525.24 and 435.96 cm^{-1} , which contributed to the Fe-O stretch vibration and Fe-OH bending vibration of $\alpha\text{-Fe}_2\text{O}_3$.^{44,45} However, several new peaks were observed after the reaction (Fig. 4b). The addition of these new peaks may be due to the adsorption of reaction products produced from oxidative decomposition of thiophene, i.e. maleic acid, CO_2 and SO_2 . It has been reported that dicarboxylic acid, like maleic acid, could be strongly adsorbed onto the surface of hematite, either by forming an interaction with one of the carboxylate groups or with both of carboxylate groups.⁴⁶ The presence of maleic acid on the hematite surface is supported by the occurrence of a sharp and distinct peak at 1739.95 cm^{-1} due to the existence of the C=O stretch (Fig. 4b). Meanwhile, a new peak at 1654 cm^{-1} ascribed to the shifted asymmetric ν_{as} (COO^-) was observed.⁴⁷ Furthermore, the broad peak at $\sim 3000 \text{ cm}^{-1}$ and sharp peak at 2972.32 cm^{-1} were clearly observed as a result of OH stretch and CH stretch of maleic acid, respectively.

Further analysis of the IR spectra of the catalyst after the reaction suggested that CO_2 was produced as the other reaction product of desulfurization thiophene in addition to maleic acid. The occurrence of CO_2 as one of the products is proven by the appearance of weak and sharp peaks at 2364.26 cm^{-1} , which corresponds to the asymmetric stretch of CO_2 .⁴⁸ It is believed that this occurrence of CO_2 is due to the further decomposition of maleic acid at high temperature during the reaction. In addition, the IR spectra also suggested that the other possible reaction product was SO_2 , which is believed to be the result of the oxidative desulfurization of thiophene in the surface of hematite. This is proven by the appearance of three strong IR absorptions at

253 wave numbers between 1300 and 1400 cm^{-1} , with features at 1375.96, 1366.08 and 1352.21 cm^{-1} ,
254 which can be ascribed as a result of adsorption of SO_2 onto the surface of the hematite
255 nanoparticles.^{49,50} Moreover, this SO_2 adsorption is also proven by the weak appearance of a
256 peak at 1511.3 and 1092.12 cm^{-1} as the result of the reaction of SO_2 and surface hydroxyl on the
257 surface of the hematite.⁴⁹ In addition, another peak around 1214.6 cm^{-1} ascribed to sulfate
258 adsorption onto the hematite surface was also observed due to the further oxidation of SO_2 on the
259 oxygen rich hematite surface.⁵¹ Furthermore, results also show that the intensity of these
260 prominent peaks also decreased with reaction time and temperature due to desorption of SO_2 and
261 sulfate from the surface (as shown in Figure 5).

262 XRD analysis was performed to investigate the crystalline phase of the catalyst before and
263 after the reaction. Figure 6 presents the XRD pattern of the catalyst collected before and after the
264 reaction. The diffraction patterns of the prior to the reaction can be unambiguously indexed as
265 the rhombohedral of hematite with no diffraction peaks for any other impurities (Fig. 6a).
266 However, Fig. 6b shows that a small amount of impurity peaks indexed as magnetite were
267 detected in the XRD pattern of the catalyst after the reaction was carried out at the
268 thiophene/water ratio of 7:3. However, these magnetite peaks disappeared when the reaction was
269 performed when the amount of water was more dominant than thiophene as the feedstock with
270 the ratio of 3:7 (as shown in Fig. 6c). These results suggest that there was a phase transformation
271 from hematite to magnetite as the result of desulfurization but it transformed back into hematite
272 when enough water was present. This phase transfer from hematite to magnetite, as discussed
273 above, resulted from the desulfurization reaction of thiophene with the lattice oxygen in hematite
274 crystals.³² No diffraction peak for magnetite was observed when the desulfurization reaction was

carried out at a thiophene/water ratio of 3:7 as more water was introduced into the reaction (Fig. 6c).

Therefore, based on the results from FTIR and XRD analysis, we know that thiophene undergoes a catalytic oxidative desulfurization on the surface of oxygen-rich hematite nanoparticles. The reaction of thiophene and oxygen on the surface of hematite nanoparticles is believed to be responsible for the thiophene oxidative decomposition as it is adsorbed onto the surface of nanoparticles. Thiophene oxidatively decomposes into maleic acid and SO_2 . As the result of this thiophene oxidation, some part of the hematite surface is reduced into magnetite, which is a form of iron oxide with a mixture of Fe^{2+} and Fe^{3+} . But, in the presence of more water in the form of steam as the source of the oxygen, a part of the hematite surfaces that were reduced into magnetite are oxidized back to hematite. The possibility of active oxygen transfer from water to catalyst surface and then finally to the feedstock (in this case thiophene) is also supported by theoretical studies since considerably little energy is required for the water splitting on the surface of magnetite.^{52,53} Hence, the overall catalytic cycle mechanism for the oxidative DS of thiophene using hematite nanoparticles can be expressed as shown in Fig. 7.

Conclusion

The catalytic activity of hematite nanoparticles has been successfully investigated and found to be catalytically active in desulfurization of thiophene. Results demonstrate that hematite nanoparticles are good catalysts for decomposing thiophene even at a low temperature of 120°C. Based on analyses, it was found that the catalytic performance of hematite nanoparticles in the desulfurization of thiophene increases with time and temperature of the reaction and the concentration of catalyst. Meanwhile, it decreases with ratio of thiophene/water and size of the

particles. Results also show that the presence of hydrogen donor (tetralin and hydrogen gas) reduced the catalytic activity of hematite due to their occupation of the hematite catalytic site without any participation in the desulfurization. Furthermore, FTIR spectra indicated that thiophene undergoes oxidative desulfurization to produce maleic acid, SO₂ and CO₂. In addition, XRD analysis revealed that the catalytic process involved a cyclic phase transformation of some of the hematite to magnetite as thiophene was oxidatively decomposed into its products, and re-oxidation of magnetite to hematite in the presence of water as the source of active oxygen.

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