Applied Catalysis B: Environmental 147 (2014) 144–155

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

The role of catalyst in supercritical water desulfurization

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ARTICLE INFO

Article history:
Received 17 April 2013
Received in revised form 23 July 2013
Accepted 9 August 2013
Available online 29 August 2013

Keywords:
Crude oil
Hexylsulfide
Dibenzothiophene
Supercritical water
Catalytic desulfurization

ABSTRACT

We evaluated supercritical water (SCW) for sulfur removal from Arabian Heavy (AH) whole crude oil and two model feeds: hexyl sulfide (HS) in hexadecane (HD) and dibenzothiophene (DBT) in HD. We measured SCW desulfurization performance in the absence and presence of ZnO, MoO_3 and MoS_2. No external hydrogen source, aside from water and oil itself, was added to the reaction mixture. SCW alone (without a catalyst) removes 6–7% of the sulfur present in AH, and addition of MoS_2 improves the sulfur removal by a factor of 2 (to ∼12%). For the HS-HD model feed, we found that HS conversion in SCW alone is high (∼85%) and is weakly affected by addition of catalysts. Hence, we infer that catalysts have minimal effect on the decomposition rates of aliphatic sulfide compounds. Addition of any of the three catalysts improved the decomposition of DBT in the HD model feed, with ZnO providing the strongest effect (from 3 to 25%). Furthermore, ZnO and MoO_3 catalysts promoted total sulfur removal, indicating a reduction in the formation of secondary sulfur compounds in the presence of oxide catalysts. We characterized the bulk and surface properties of fresh and SCW-exposed catalysts for treatment of the HS-HD model system using X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectrometry (XPS). As anticipated, MoS_2 remained unchanged during the SCW treatment, whereas MoO_3 and ZnO underwent structural and morphological changes primarily related to sulfidation reactions. The results of this work help establish the role of catalysts in the SCW process; demonstrate that modest desulfurization can be achieved in the absence of an external hydrogen source; and provide guidelines for catalyst selection.

1. Introduction

The removal of sulfur-containing compounds from crude oil is increasingly important due to steady increases in the sulfur content of remaining petroleum resources and mounting environmental concerns associated with SO_X emissions. The primary sulfur removal method is hydrodesulfurization (HDS), a process that has long been used at the refinery level [1–3]. Refining high sulfur feeds to meet increasingly stringent sulfur requirements has placed stress on the performance of HDS, especially due to the costs of the large amounts of required hydrogen. For this reason, hydrogen-free sulfur removal processes have received substantial interest in the last decade [4]. Hydrogen-free sulfur removal methods include oxidation desulfurization (ODS) [5–8], oxidation–extraction desulfurization (OEDS) [9–11], adsorption desulfurization (ADS) [12–16] and bio-desulfurization (BDS) [17–19]. None of the options to HDS has been proven economically viable at commercial scales, motivating continued efforts to identify hydrogen free methods to reduce sulfur content.

Supercritical water (SCW) treatment is a potential sulfur removal technique that is particularly beneficial for treating heavy oils [20–24]. SCW is a good solvent for promoting heteroatom removal, as both C—O (as in ethers) and C—S bonds (as in sulfides) are cleaved more easily in SCW than they are under conventional "dry" pyrolysis conditions [25–31]. Furthermore, SCW is a non-polar solvent that has the ability to dissolve organic compounds, which includes the majority of components in crude oil, as well as "permanent gases". In certain cases, reaction rates and product distribution in reactions performed in SCW can be manipulated by adjusting reaction conditions, e.g., temperature, pressure, reactants concentration, and catalysts [32]. SCW has a viscosity comparable to a gas, which accelerates mass transfer processes relative to their liquid phase rates and allows some catalysts to retain high activity for extended periods of time [25,32,33]. However, SCW is a

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http://dx.doi.org/10.1016/j.apcatb.2013.08.018

chemically aggressive environment, which can rapidly de-activate many catalysts, so they must be selected carefully [34–38].

Upgrading heavy oils using SCW has been described in a few U.S. patents, which claim that the process can be performed without addition of catalysts or external hydrogen sources [39–41]. Lin et al. [39] used SCW in the absence of an external hydrogen source, without a catalyst, to upgrade hydrocarbons and obtained products with highly desirable properties, such as low sulfur and metal contents, lower density and viscosity, and lower residuum contents. In a similar study, Choi and Al-Shareef used an ultrasonic wave generator and hot pressurized water to upgrade Arabian heavy crude oil [40]. In contrast, a SCW process reported by Banerjee to upgrade extra heavy crude oil required addition of either hydrogen or CO and the presence of an alkali-salt promoted zirconium or iron oxide catalyst [41]. A landmark academic study on the desulfurization and de-metalization of gas oil in SCW showed that, without addition of hydrogen and catalysts, SCW is not sufficient for upgrading sulfur-spiked gas oil [42]. Furthermore, Adschiri et al. [43,44] have systemically investigated the hydrothermal cracking of dibenzothiophene (DBT) in SCW in the presence of NiMo catalysts at pressures and temperatures as great as 30 MPa and 703 K, respectively. They found that desulfurization required the addition of a hydrogen carrier such as molecular hydrogen, CO, CO_2/H_2, or HCOOH.

The literature discrepancies on the effectiveness of the SCW process may be due in part to differences in the sulfur compounds that were studied by the different research teams. Indeed, different sulfur group types respond differently to the SCW process. Non-aromatic sulfur compounds, including sulfides and thiols, cleave easily in SCW, whereas, compounds with sulfur in an aromatic ring are more stable [20,28,29]. Therefore, SCW desulfurization of aromatic sulfur compounds may require addition of either a catalyst or other additives [42,43,45]. However, because of the poisoning effect of sulfur for metal catalysts, aggregation and dissolution of solid materials, and oxidation of metal components in SCW, only a limited range of catalytic materials can be used in the process [36,46,47]. In addition, conventional catalyst support materials, such as silica and alumina, severely degrade in the SCW reaction environment [46]. Catalyst stability under SCW conditions has been the focus of only a handful of studies, most of them focused on biomass gasification conditions [37,48,49] rather than sulfur removal conditions relevant to petrochemical processes [34–36,46]. In SCW gasification studies, three types of heterogeneous catalysts, including activated carbon, transition metals, and their oxides, have been used to promote SCW gasification [37,48]. In particular, the oxides of Ce, Co, Fe, Mn, Ti, Mo, and Zn have been commonly used as catalysts in SCW [47].

In this work, we studied the effect of several low-cost catalysts on SCW desulfurization of three types of sulfur-containing feeds, including Arabian heavy crude oil and hexadecane (HD) mixtures of hexyl sulfide (HS) and dibenzothiophene (DBT), in the absence of an external hydrogen source. We evaluated MoS_2, a traditional HDS catalyst; MoO_3, the oxide of an HDS catalyst; and ZnO, which is an H_2S adsorbent that has been used for reactive adsorption of sulfur. These catalysts were tested for activity, stability, and chemical mechanism elucidation.

2. Experimental

In their reviews of heterogeneous catalysis in SCW, Savage [38] and later Yeh et al. [37] cited a need for greater understanding of the catalyst stability, including morphological changes that occur in SCW at different conditions. Moreover, the SCW upgrading of crude oil is particularly challenging given that the catalyst must be stable in the presence of water and sulfur, both of which degrade the catalyst but via different mechanisms. Much of our knowledge on catalyst stability in SCW is from the work on SCW gasification [50] on low-sulfur biomass feeds, as reported originally by Pacific Northwest National Laboratory [49]. For this reason, a study that probed catalyst stability at SCW conditions in the presence of a sulfur rich feed was needed. We selected 3 materials for our preliminary study – MoS_2, MoO_3, and ZnO. Each of these materials is available at low cost; Table 1 explains the selection of each material and some of their properties. Conveniently for purposes of comparison, the initial BET surface areas and pore volumes of the catalysts were similar to one another, all in the range from 7 to 10 $m^2\,g^{-1}$ and 0.041 to 0.052 $cm^3\,g^{-1}$, respectively. In terms of expected performance, MoS_2 is a known HDS catalyst, whereas ZnO is a known H_2S adsorbent. H_2S has well documented effects on chemical reactivity [51] and we were interested if H_2S removal might alter SCW desulfurization. Moreover, we wanted to investigate 1) the influence of H_2S removal on the formation of “secondary” sulfur compounds and 2) the use of ZnO as a “co-catalyst” to protect a second, more active catalyst from H_2S poisoning. Finally, MoO_3 was selected as a sulfur adsorbent that would be sulfided into a form with potential catalytic activity (MoS_2). Previous work had shown that sulfidation of MoO_3 produced a high-surface-area MoS_2 that might prove to have high catalytic activity [52–55].

To study both sulfur- and water-rich conditions, we investigated catalyst performance and stability for three feeds: 1) Arabian Heavy (AH), 2) model hexadecane oil containing 3 wt% hexyl sulfide (HS-HD), and 3) model hexadecane oil containing 0.1 wt% DBT (DBT-HD). Table 2 summarizes the experiments and their selection rationale. Arabian Heavy was selected to test performance for a real feed with high sulfur content. DBT-HD was selected because DBT is well known to be highly refractory to HDS and is present in modest quantities in AH. However, because the solubility of DBT in HD at room temperature is low, we studied a 0.1 wt% solution (on a sulfur basis). HS-HD was selected to re-produce the high sulfur conditions present for treatment of AH. Additionally, HS-HD is known to decompose rapidly to produce H_2S in near- and SCW to yield H_2S [27,56] and we were particularly interested in probing the effects of H_2S on catalyst stability without the hazards of handling and storing pressurized H_2S cylinders.

2.1. Materials

Di-n-hexyl sulfide (HS, 97% purity) and dibenzothiophene (DBT, 99% purity) were purchased from Alfa-Aesar and Aldrich, respectively. Hexadecane (HD, 99% purity) was purchased from Sigma–Aldrich. The catalysts were obtained from Sigma–Aldrich: zinc oxide (ZnO, ACS reagent, ≥99.0%, p/n 251607), molybdenum (VI) oxide (MoO_3, ACS reagent, ≥99.5%, p/n 267856), and molybdenum (IV) sulfide (MoS_2, powders with particle size of ~6 μm, p/n 69860). Arabian heavy (AH) crude oil was obtained from Saudi Aramco Company. Table 3 lists some relevant characteristics of the feed [57]. SARA (Saturates-Aromatics-Resins-Asphaltenes) analysis was performed using an HPLC technique, similar to that published in the literature [58]. All chemicals were used without further purification. Water was de-ionized (DI) to a resistivity of 18.1 $M\Omega$ cm immediately prior to use.

2.2. Apparatus and reaction runs

All runs were carried out in a 316-stainless steel batch microreactor (24 ml in volume) obtained from High Pressure Equipment Company (p/n MS-16) and equipped with a 316-stainless steel cross for connecting the reactor to a pressure transducer, a gas feed/collection port, and a rupture disk for safety. Heating was provided by a fluidized sand bath (Techne Industrial, p/n FB-08) with a temperature control precision of ±0.5 °C. For all runs, temperature