Fuel Processing Technology 116 (2013) 44–51

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

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

Deep desulfurization of gas oil over NiMoS catalysts supported on alumina coated USY-zeolite

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ARTICLE INFO

Article history:
Received 8 January 2013
Received in revised form 10 April 2013
Accepted 13 April 2013
Available online xxxx

Keywords:
Gas oil
Deep hydrodesulfurization
Alumina
Y-zeolite
Two-stage processing

ABSTRACT

A series of NiMoS catalysts supported on USY-zeolite coated with different amounts of alumina were prepared and evaluated for deep hydrodesulfurization (HDS) of gas oil using a flow reactor system in single- and dual-bed configurations. The performance of these catalysts was compared to the conventional HDS catalyst as well as to NiMoS catalyst supported on physical mixture of alumina and USY-zeolite. Physically mixed alumina and USY zeolite showed high HDS activity, but it was accompanied with significant cracking of hydrocarbons. Activity and kinetic analysis showed that heavy coating of alumina on the zeolite resulted in much lower HDS and cracking activity. On the other hand, very light coating of alumina on the zeolite resulted in catalytic behavior similar to that of physical mixture of USY-zeolite and alumina. The general trend was an increase in HDS as well as hydrocracking activity with the decrease in amount of alumina coating over zeolite. Changes in product density, aromatic content, mid-boiling point, cetane index, and molecular weight also reflected this trend. The results of this study indicate that catalysts with neither too low nor too high amount of alumina coating on the USY zeolite are suitable to achieve the balance between high HDS and low cracking activities. The highlight of the present study is that it confirmed the deep HDS activity of USY containing alumina supports in the flow reactor system which is industrially applied. In addition, the stability test confirmed the long-term performance of alumina-coated zeolite catalyst.

1. Introduction

Deep hydrodesulfurization (HDS) of gas oils continues to attract research interest due to increasing demand of diesel fuel as well as environment-driven regulations which limit its sulfur content to 10–15 ppm [1,2]. Several studies have shown that the sulfur compounds that remain in the diesel fuel after conventional HDS are mainly dibenzothiophenes (DBTs), especially those with alkyl substituents at the 4 and 6 positions. Removal of these refractory sulfur compounds is necessary to achieve the specifications of ultra-low sulfur diesel. The removal of such refractory sulfur species proceeds via two parallel pathways: the direct desulfurization pathway (DDS) and the hydrogenation pathway (HYD) [3,4]. The former pathway requires severe process conditions to overcome the steric hindrance, while the latter pathway undergoes hydrogenation of neighboring phenyl group prior to C–S bond scission. Although the hydrogenation of refractory sulfur species occurs under rather mild process conditions, it competes with the reactions of nitrogen and aromatic species as well as other sulfur species.

The widely used Ni(Co)Mo(W) catalytic system supported on γ-alumina for the conventional hydrodesulfurization (HDS) serves well for the removal of reactive sulfur species. However, major improvements in catalysts are required, especially for deep HDS of gas oils derived from heavy crudes. Hence, novel catalyst formulations and process designs need to be developed [5,6]. Among the possible innovations in the catalyst formulation is the chemical and physical modification of supports to activate the metal sulfide species for deep HDS of gas oil by improved dispersion. Furthermore, such modified supports can also adsorb some of the feed molecules to activate and transfer them to the sulfide catalyst through the spillover and reverse spillover mechanisms. The acidic supports have been reported to perform such roles efficiently [7–10]. Thus development of improved acidic supports is considered as a viable means to design high-activity catalyst for deep HDS of gas oil.

Different types of zeolites have been used as acidic supports for the molybdenum sulfide catalyst and they are reported to exhibit higher activity for the HDS of refractory sulfur species as well as resistance towards H_2S resistivity. Rozanska et al. [11,12] reported that

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http://dx.doi.org/10.1016/j.fuproc.2013.04.012

pure zeolite alone can hydrodesulfurize DBT through both the direct elimination of sulfur atom and HYD-DDS routes. However, extensive cracking of gas oil feed and rapid deactivation of its acidic sites are critical issues for such pure zeolite catalyst [3,10]. Combining the conventional supports and acidic zeolites may offer combination of desirable properties and can provide a very promising approach for deep HDS [13–17]. Physical mixture of alumina and USY zeolite has been reported as an excellent support for NiMoS possessing high HDS activity and resistivity against H_2S as high as 1.67% in H_2 [9,18–22]. The reason for higher cracking reactivity of alumina-zeolite supported metal sulfide catalyst was attributed to the exposed surface of zeolite. However, activity of exposed zeolite can be quickly lost through the rapid coking. In an earlier study [23], we have investigated surface modification of USY-zeolite with alumina to maintain high HDS activity with the least cracking activity.

In this study, a series of NiMoS catalysts were prepared with zeolite supports which were coated with different amounts of alumina. HDS activity and influence on product density, mid-boiling point, aromatic content and molecular weight was determined using a fixed-bed, flow reactor under industrial process conditions in single- and the dual-bed configurations. A 3000–4000-hour catalyst stability test was carried out to estimate the deactivation under industrial process conditions.

2. Experimental

2.1. Catalysts

USY-zeolite (Si/Al ratio = 30) was prepared from commercially available Na-Y precursor. Alumina in Na-Y precursor was extracted by an acid in order to obtain high silica/alumina ratio in the zeolite network having suitable solid acidity and hydrothermal stability. Particle size of USY-zeolite was 1.5–2.0 μm in hexagonal shape with a surface area of 650 m^2/g. Zeolite-based catalyst support was prepared by mechanical mixture of aluminum hydroxide (as matrix) and USY-zeolite in equal proportions. This mixture was coated with porous aluminum hydroxide using a neutralization procedure through which the amount of coating was controlled. The coating material was converted into γ-alumina through calcination. Five alumina-coated supports with different amounts of coating were prepared in this manner. The amount of alumina used for coating is quite low compared to the bulk of the catalyst support. However, actual content of alumina in the bulk could not be verified because it was not possible to distinguish the alumina in matrix from coating. Hence, the bulk composition of the catalyst supports can be considered about 50% USY zeolite and the remaining as alumina.

The catalyst supports were identified as follows:

(i) AZ (physical mixture of alumina and USY zeolite); and
(ii) CZ-1 to CZ-5 (alumina-coated zeolites with increasing amount of coating).

The zeolite containing supports were impregnated with MoO_3 (15%) and NiO (5%) for the preparation of the catalysts. The catalyst having physical mixture of alumina and USY is named as AZ, whereas the five catalysts supported on alumina-coated zeolites are named as CZ-1 to CZ-5 with increasing amount of alumina coating.

2.2. Characterization of catalysts

The physical characteristics of the catalysts, such as BET total surface area, pore volume and pore size, were evaluated using nitrogen adsorption method at 77 K, measured with BELSORP-Max-S (Nippon BEL Inc. Japan). Prior to the measurements, catalysts were degassed at 150 °C for 10 h.

Temperature programmed desorption (TPD) of NH_3 was performed to measure total acidity, which includes Brönsted and Lewis acidic sites, of the oxide forms of the catalysts by using a TPD-1-AT (BEL, Japan), equipped with a quadrupole mass spectrometer (QMS) as a gas analyzer. For this purpose, 50 mg of powder catalyst sample was dried at 110 °C for 24 h in an oven. The catalyst was packed in the quartz cell, heated to 400 °C (10 °C/min) and kept at the temperature for 30 min under He flow before the exposure to 5 vol.% NH_3 in He at 25 °C for 30 min. The desorbed NH_3 was measured from 25 °C to 627 °C at the heating rate of 10 °C/min after removing weakly absorbed NH_3 by heating the catalyst sample to 100 °C and then cooling it down to 25 °C under pure He flow.

The crystallographic characteristics of the catalysts were evaluated using X-ray diffraction (Rigaku UltimaIII, CuKα target, Rigaku, Japan). Data were collected using a continuous scan mode with a 2-theta range of 5° and 70° and a scan rate of 2°/min.

2.3. Catalyst performance evaluation

Catalytic activity for the HDS of typical straight-run gas oil (SRGO) was determined in a fixed-bed flow reaction system. The properties of SRGO feedstock are presented in Table 2. The pilot unit included two high-pressure fixed-bed reactors in series, pressure controller, high-pressure feed pump, mass flow controller to adjust inlet gas flow, and high pressure gas–liquid product separator. The reactors were heated to the required temperatures by electric furnace. The temperature of each reactor was individually controlled and monitored by separate thermocouples placed in the catalyst bed in each reactor. Tubular reactors were loaded with catalyst in each reactor. The catalysts were tested in the single- and the dual-bed configurations. For the dual-bed configuration, the first reactor was loaded with a LX6 (50 vol.% of the total catalyst volume) while the second reactor was loaded with either AZ or one of the CZ-*i* catalysts (50 vol.%). LX6 is a commercial $CoMo/Al_2O_3$ catalyst, which has been reported to be an active catalyst for the desulfurization of reactive sulfur species to 50 ppm under industrial process conditions.

Prior to performance testing, the catalyst was presulfided *in-situ* using a spiked feed (gas oil mixed with a presulfiding agent SulfrZol®54, S content = 2.0 wt.%). The LHSV of spiked feed was 1.0 h^{-1} under H_2 pressure of 5 MPa and H_2/oil ratio of 200 Nm^3/m^3. During presulfiding, the temperature was increased from ambient to 320 °C at a rate of about 25 °C/h and maintained for 10 h.

The gaseous feed to the pilot unit was 90 vol.% H_2/10 vol.% N_2 gas mixture. To start a catalyst performance test, gaseous feed and SRGO were introduced concurrently from the top of the reactor. The performance of catalysts was evaluated at 330, 345, and 360 °C while the LHSV (1.0 h^{-1}), H_2 pressure (6 MPa) and H_2-to-oil ratio (250 Nm^3/m^3) were kept constant. After about 3 h of steady-state once-through operation, liquid product samples were collected. The dissolved H_2S in liquid product was removed in a specially-designed stripper with N_2 flowing through a sintered metal. Gaseous products were also collected and analyzed. A 3000–4000 catalyst stability test with LX6/AZ and LX6/CZ-1 catalyst combination was also carried out to estimate the deactivation under practical conditions.

2.4. Feedstock and product analysis

Total sulfur of the feedstock and hydrotreated products was determined by Ultra-Violet Fluorescence method and total nitrogen was measured by chemical luminescence method (TS-100V, Mitsubishi Chemical Analytech Co., Ltd.). The density of the feedstock and hydrotreated products was analyzed using a density meter (DA-500, Kyoto-Densi). The aromaticity was determined by gas chromatograph (GC 353B-FID GL Science) equipped with a supercritical CO_2 carrier and FID detector. Carbon and sulfur species and their distributions were analyzed using a gas chromatograph (GC, HP6890+, Agilent) coupled with an atomic emission detector (AED, G2350A, JAS). Details of analysis using GC-AED are reported elsewhere [24]. GC simulated distillation was carried out to measure the boiling point distribution