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ScienceDirect

Fuel 87 (2008) 2343–2346

www.fuelfirst.com

Short communication

Hydrodesulfurization and hydrodearomatization activities of catalyst containing ETS-10 and $AlPO_4$-5 on Daqing FCC diesel

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Received 1 March 2007; received in revised form 20 October 2007; accepted 26 October 2007
Available online 20 November 2007

Abstract

A Ni–W loaded ETS-10/$AlPO_4$-5/Al_2O_3 composite support catalyst was optimized and used in hydrodesulfurization (HDS) and hydrodearomatization (HDA) of Daqing FCC diesel feedstock. The result indicated that ETS-10 and $AlPO_4$-5 showed positive synergism effect. The effects of operating conditions on its catalytic performance were investigated by using a 100 mL hydrotreating test unit. The catalyst showed a remarkable HDS conversion of 99.9% and a HDA conversion of 73.2%. A clean diesel product with ultra-low sulfur content (<1.0 μg/g) and very low polycyclic aromatic content (<2.0 wt.%) was obtained.

Keywords: ETS-10/$AlPO_4$-5; HDS/HDA; Ultra-low sulfur diesel

1. Introduction

Hydrotreating catalysts are playing an important role in the modern refinery to produce clean fuel [1–3]. However, it is a big challenge for conventional hydrotreating catalyst to produce ultra-low sulfur and low aromatic diesel [4]. Therefore, it is imperative to develop more active and more selective hydrotreating catalyst for hydrodesulfurization (HDS) and hydrodearomatization (HDA) [5–9].

In the course of our effort to improve the performance of HDS/HDA catalyst, a novel composite support, the unique combination of titanosilicate ETS-10 with good thermal stability [10–13] and aluminophosphate $AlPO_4$-5 of crystalline $AlPO_4$ structure [14] with alumina, was firstly developed, and the tailoring effects of ETS-10 and $AlPO_4$-5 to alumina, as well as the promotions for HDS and HDA with a Ni–W based model catalyst were reported [13,15–19]. In the present paper, we would like to report the investigations on the optimization of ETS-10 and $AlPO_4$-5 containing hydrotreating catalyst by using real FCC diesel as feedstock. The HDS/HDA performances of this catalyst with alternated operating conditions by using a 100 mL hydrotreating test unit are also presented.

2. Experimental

A typical procedure for catalyst preparation is as follows, the even mixture of ammonium-exchanged ETS-10 [13], $AlPO_4$-5 [16] and pseudo-boehmite powder was extruded, followed by drying at 393 K for 4 h and calcining at 823 K for 4 h. The obtained composite support was designated as ATSP. For comparison, the composite supports containing ETS-10 or $AlPO_4$-5 merely, designated as AETS or AAP, respectively, were also prepared under the similar procedure. The catalysts NiW/ATSP, NiW/AETS, NiW/AAP and NiW/Al_2O_3 with the same Ni–W loading amounts of metal (28.9 wt.% of WO_3 and 5.0 wt.% of NiO) were prepared by pore volume impregnation method and catalysts were designated as C-ATSP, C-AETS, C-AAP and C-Al_2O_3, respectively. The HDS and HDA activity were evaluated in a continuous flow fixed-bed reactor

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doi:10.1016/j.fuel.2007.10.022

with the catalyst loading of 100 mL. The catalysts were presulfided in situ with 2 vol.% CS_2 in kerosene. The feedstock, Daqing FCC diesel, have density of 0.8702 g/mL, sulfur content of 1052.0 μg/g and total aromatic content 51.2 vol.%.

The total sulfur content was measured by a coulometric sulfur analyzer. The total aromatic content analyses were determined by the standard method of fluorescence indicator adsorption by using Dalian TSY-1132 instrument. The composition was analyzed by BOMEM MB-160 near infrared (NIR) spectra.

3. Results and discussion

3.1. Effect of support composition on catalyst activity

The catalyst activities of C-Al_2O_3, C-AETS, C-AAP and C-ATSP at 8.0 MPa, 633 K, 1.0 h^{-1} and 500:1 (H_2/oil, v/v) are listed in Table 1. It was obvious that the catalytic activity of the catalysts containing ETS-10 or $AlPO_4$-5 was enhanced in comparison with that of C-Al_2O_3. In detail, compared with catalyst C-Al_2O_3, HDS and HDA conversions increased by 1.4% and 2.8% for catalyst C-AETS, and increased by 0.5% and 5.7% for catalyst C-AAP. This indicated that catalyst containing $AlPO_4$-5 (catalyst C-AAP) showed better HDA activity than the catalyst containing ETS-10 (catalyst C-AETS), whereas, the HDS activity of catalyst C-AETS was better than that of C-AAP. The difference of activity and selectivity for C-AETS and C-AAP may be resulted from the different characteristic of molecular sieves ETS-10 and $AlPO_4$-5 [17,18]. Thus, when various amount of ETS-10 or $AlPO_4$-5 were introduced to alumina to prepare the corresponding composite support, the different degree of influences on the dispersion of metal active component could be caused. The data in Table 1 indicates that the catalyst C-ATSP (containing both $AlPO_4$-5 and ETS-10) owns the highest HDS (conversion 99.7%) and HDA (conversion 72.9%) activities. It reduced the sulfur content from 1052.0 μg/g to 2.7 μg/g, and aromatics from 51.2 vol.% to 13.9 vol.%. It was clear that simultaneous introduction of ETS-10 and $AlPO_4$-5 at a proper ratio could not only take advantage of their individual advantages (HDS or HDA), but also cause positive synergism effects amidst them, which results in a remarkable enhancement in the catalytic activity of the catalyst C-ATSP.

Table 1
The HDS and HDA activities of C-Al_2O_3, C-AETS, C-AAP and C-ATSP under conditions of 8.0 MPa, 633 K, 1.0 h^{-1}, 500:1 (H_2/oil, v/v)

Catalyst	HDS conversion (%) (Sulfur content, μg/g)	HDA conversion (%) (Aromatic content, vol.%)
C-Al_2O_3	97.6 (25.6)	56.4 (22.3)
C-AETS	99.0 (10.2)	59.2 (20.9)
C-AAP	98.1 (19.5)	62.1 (19.4)
C-ATSP	99.7 (2.7)	72.9 (13.9)

Note: HDS conversion (%) = $[(S_{\text{feed}} - S_{\text{product}})]/S_{\text{feed}} \times 100$; HDA conversion (%) = $[(A_{\text{feed}} - A_{\text{product}})]/A_{\text{feed}} \times 100$. Where S_{feed} and S_{product} are the total sulfur contents (m%) in the feedstock and liquid product, respectively, and A_{feed} and A_{product} are the total aromatic contents (vol.%) in the feedstock and liquid product, respectively.

The evaluation data showed that decreasing ETS-10/$AlPO_4$-5 ratio would result in the increase of HDS and HDA conversions and the highest HDS and HDA conversions achieved were 99.7% and 72.9% for catalyst C-ATSP, in which the ratio of ETS-10 to $AlPO_4$-5 was 1:2 (wt/wt). It was found that the introduction of ETS-10 and $AlPO_4$-5 can also bring a certain amount of moderate Brönsted acid sites [19], which favor eliminating the refractory 4,6-DMDBT and its steric-hindered derivatives through the isomerization-hydrogenation pathway.

Table 2 compares the NIR compositional analysis data of Daqing FCC diesel before and after hydrotreating over C-ATSP catalyst. The content of alkanes in hydrotreated diesel increased by 12%, which may mainly result from saturation of olefins, saturation and ring opening of monoaromatics with short side chain, and ring opening of single ring cycloparaffin. It is known that reaction rate constant of diaromatics and triaromatics was far greater than that of monoaromatics. In the present work, the content of polycyclic aromatics (diaromatics and triaromatics) decreased from 33.1 wt.% to 4.6 wt.%, and accordingly, the calculated Cetane Number increased from 26.7 to 47.7.

3.2. Effect of reaction conditions on HDS and HDA activities

HDS and HDA activities of C-ATSP catalyst were investigated at various reaction temperatures (573 K, 593 K, 603 K, 613 K, 623 K, 633 K and 643 K) at 8.0 MPa, 1.0 h^{-1}, 500:1 (H_2/oil, v/v). HDA conversion increased with temperature elevating from 19.8% (573 K) until 68.8% (633 K), after 633 K it turned to decrease. HDS conversion also increased with temperature elevating from 99.2% (573 K) until 99.9% (603 K). No further HDS conversion increasing was observed when higher temperature was used. The NIR compositional analysis data of the hydrotreated diesel products over catalyst C-ATSP at temperature range from 573 K to 613 K also suggest that

Table 2
Comparison of the compositional NIR analysis of FCC diesel feed and the hydrotreated diesel over catalyst C-ATSP under the conditions of 8.0 MPa, 633 K, 1.0 h^{-1}, 500:1 (H_2/oil, v/v)

Item	FCC diesel feed	Product
Saturates (wt.%)	40.7	68.9
Alkanes (wt.%)	27.9	39.7
Cycloalkanes (wt.%)	13.0	26.5
Monocycloalkanes (wt.%)	11.0	10.4
Dicycloalkanes (wt.%)	1.8	10.3
Tricycloalkanes (wt.%)	0.4	7.1
Aromatics (wt.%)	58.6	31.2
Monoaromatics (wt.%)	24.2	26.7
Diaromatics (wt.%)	27.6	3.9
Triaromatics (wt.%)	5.5	0.7
Calculated cetane number	26.7	47.7