Selectivity enhancement of $CoMo/Al_2O_3$ catalyst in the hydrodesulfurization of FCC gasoline

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Abstract: Traditionally prepared $CoMo/Al_2O_3$ catalyst, although efficient for deep desulfurization, is not appropriate in the HDS of FCC gasoline due to its high hydrogenation activity of olefins especially when the HDS conversion is high. Herein, we report the CoMo supported on three alumina with different properties. The $CoMo/Al_2O_3$-3 catalyst with the highest HDS selectivity show superior performance in the HDS of a real heavy FCC gasoline. The RON loss is only 1.0 unit when the sulfur content in the product is 10 ppm.

Keywords: Alumina, FCC gasoline, Selective hydrodesulfurization.

1. Introduction

The traditional hydrotreating catalysts $Co(Ni)Mo(W)/Al_2O_3$ possess both HDS and hydrogenation (HYD) active centers. Under the typical reaction conditions, the deep desulfurization will result in inevitable a huge research octane number (RON) loss because of the heavy HYD of olefins with high octane number. Therefore, the best way to solve this problem is to develop a highly selective catalyst.

2. Experimental

Three different alumina supports denoted as Al_2O_3-1, Al_2O_3-2 and Al_2O_3-3 were prepared. The corresponding CoMo supported catalysts denoted as $CoMo/Al_2O_3$-1, $CoMo/Al_2O_3$-2 and $CoMo/Al_2O_3$-3 were prepared by the successive incipient wetness impregnation method with the same MoO_3 and CoO loading. The catalysts were evaluated on a high-pressure fixed-bed continuous flow microreactor using a real full-range FCC gasoline. The reaction was carried out at 250-280 ^oC, 1.5 MPa, H_2/oil ratio of 300 Ncm^3/cm^3, WHSV 5.3 h^{-1}, 0.5 g catalysts. Finally, according to, the HDS activity (HDS%), hydrogenation activity of olefins (HYD%) and the selectivity factor (SF) were calculated as follows:

$$\mathrm{HDS\%} = \frac{S_f - S_p}{S_f} \times 100 \quad \mathrm{HYD\%} = \frac{O_f - O_p}{O_f} \times 100 \quad \mathrm{SF} = \frac{\ln(S_f / S_p)}{\ln(O_f / O_p)}$$

Where the S_f and S_p represent the mass fractions of total sulfur content in the feedstocks and products, and O_f and O_p are the volume fractions of total olefin content in the feedstocks and products.

A scale up test was also done using 10 ml $CoMo/Al_2O_3$-3 catalyst and a heavy FCC fraction as the feedstock. The heavy FCC fraction has a sulfur content of 309 ppm, olefin content of 16.83 v% and RON value of 85.7.

3. Results and discussion

As listed in Table 1, the HDS selectivity increased in the order of $CoMo/Al_2O_3$-1 < $CoMo/Al_2O_3$-2 < $CoMo/Al_2O_3$-3. Especially, when the reaction temperature was elevated to make the $CoMo/Al_2O_3$-3 has the same HDS conversion of $CoMo/Al_2O_3$-1, the HYD activity of $CoMo/Al_2O_3$-3 was still 15% lower than $CoMo/Al_2O_3$-1. Furthermore, the scale up HDS test of $CoMo\text{-}Al_2O_3$-3 using a heavy FCC gasoline as feedstock showed that the RON loss is only 1.0 unit when the sulfur content was reduced to 10 ppm, which is very promising for industrial application.

Catalyst	Sulfur (ng/ul)	HDS(%)	Olefin (v%)	HYD(%)	SF	RON loss
Feed	257.7	\	22.20	\	\	\
$CoMo/Al_2O_3$-1[a]	38.9	84.9	17.65	20.5	8.2	\
$CoMo/Al_2O_3$-2[a]	26.1	89.9	17.78	19.9	10.3	\
$CoMo/Al_2O_3$-3[a]	59.5	76.9	19.80	10.8	12.8	\
$CoMo/Al_2O_3$-1[b]	22.1	91.4	16.11	27.4	7.7	\
$CoMo/Al_2O_3$-2[b]	18.5	92.8	16.30	26.6	8.5	\
$CoMo/Al_2O_3$-3[b]	34.9	86.5	18.68	15.9	11.6	\
$CoMo/Al_2O_3$-1[c]	12.6	95.1	12.82	42.3	5.5	3.3
$CoMo/Al_2O_3$-2[c]	10.9	95.8	13.06	41.2	6.0	3.2
$CoMo/Al_2O_3$-3[c]	18.9	92.7	17.49	21.2	11.0	1.8
$CoMo/Al_2O_3$-3[d]	12.8	95.0	16.16	27.2	9.5	2.3

[a] 250 °C, 1.5 MPa, WHSV 5.3 h^{-1}, and H_2/oil ratio of 300 Ncm^3/cm^3.

[b] 260 °C, [c] 270 °C, [d] 280 °C, the other conditions are the same.

Table 1. Catalytic properties of the CoMo oxide catalysts in HDS of a full-range FCC gasoline

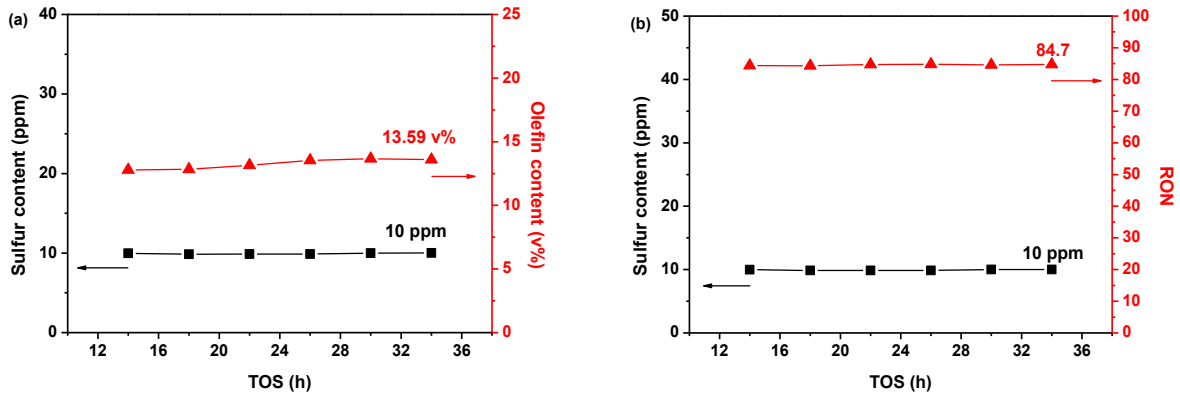

Figure 1. Total sulfur content and olefins content (a), RON value (b) of the product with the heavy fraction of FCC gasoline as feedstock. Reaction conditions: 280 °C, 1.5 MPa, H_2/oil ratio of 300 Ncm^3/cm^3, LHSV 3 h^{-1}.

4. Conclusions

In this work, the HDS selectivity of $CoMo/Al_2O_3$ catalyst was greatly improved by tailoring the properties of the alumina support. The sulfur content could be reduced to 10 ppm while the RON loss is only 1.0 unit by $CoMo/Al_2O_3$-3 in the HDS of a heavy FCC fraction, which is promising for industrial application.

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