Study on the Effect of Sulphur and Nitrogen Content of Gas Oil on the Hydrodearomatization Activity of Pt-Pd/USY Catalyst

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In this study, hydrodearomatization (HDA), hydrodenitrogenation (HDN) and hydrodesulphurization (HDS) of real gas oils (various sulphur, nitrogen and total aromatic content) was investigated over Pd, Pt catalysts supported on USY zeolite. The effect of sulphur and nitrogen content of feeds on HDA, HDN and HDS activities was studied. Additionally, the effect of key process parameters (temperature, pressure, LHSV, H_2/hydrocarbon volume ratio) on the yield and quality of products was also investigated. Summing up the results, the investigated catalyst (Pt-Pd/USY) provided high HDA, HDS and HDN activities in presence of sulphur and nitrogen in feed. That's why high sulphur (up to 300 mg/kg) and nitrogen (up to 200 mg/kg) content can be upgraded to high quality (low sulphur, nitrogen and aromatic content) blendstocks for diesel fuel in the hydrodearomatization pressure range (45-60 bar) in one step.

1. Introduction

Sulphur content of diesel fuels has been reduced in a large extent in the past decade all over the world. In the European Union the maximum allowable sulphur content is 50 mg/kg at present. Additionally the availability of diesel fuels of sulphur content of 10 mg/kg should be ensured, and sulphur content of all diesel fuels has to be maximum 10 mg/kg after 1st January, 2009 (Pölczmann, 2007). Reduction of the aromatic content of diesel fuels is also relevant, because aromatic hydrocarbons have low cetane number, contributing to the increase of vehicle emission (mainly the hydrocarbon and particulate matter). For these reasons, in recent years, sulphur and nitrogen tolerant (up to 50-200) precious metal catalysts have attracted much attention for the hydrogenation of aromatics in diesel fuels (Varga, 2005). Unfortunately, for the noble metal catalysts (e.g. Pt or Pd), the sulphur content in the feedstock must be strictly reduced before the catalyst comes in contact with the feedstock (Bihan, 2002). Bimetallic catalysts (e.g. Pt-Pd/USY) and/or acidic support can be used to increase the sulphur tolerance. In general, the sulphur tolerance of noble metal catalysts increases with electron deficiency of noble metal particles (Matsui, 2005). In addition to the sulphur tolerance of noble metal catalysts, their tolerance to nitrogen is an important issue because most petroleum feedstocks contain nitrogenous compounds (Matsui, 2005, Revellin, 2005). However, acidic supports, which increase the sulphur tolerance of noble metal phase due to electron transfer (electron deficiency of noble metal particles), are subject to poisoning by nitrogen-containing compounds, including NH_3 (Yoshimura, 2001, Yasuda, 1999). The inhibiting effect of nitrogen compounds on the sulphur tolerance have been investigated, but the presence of strongly acidic sites in some cases makes the nitrogen-tolerance of noble metal catalysts more complicated (Matsui, 2005). Previous study reported that a bimetallic Pd-Pt catalyst supported on ytterbium-modified ultrastable (USY) zeolite was effective for deep hydrodesulphurization (HDS) and deep hydrodearomatization (HDA) and was stable in the presence of sulphur and nitrogen (Pettito, 2002, Shimada, 2003).

In this work we investigated the catalytic performance of Pd-Pt/USY zeolite catalysts in hydrogenation of real gas oils as feedstocks with different sulphur and nitrogen content. The effect of sulphur and nitrogen content of feeds on HDA, HDN and HDS activities was studied. Additionally, the effect of key process parameters (temperature, pressure, LHSV, H_2/hydrocarbon volume ratio) on the yield and quality of products was also investigated.

2. Experimental

Apparatus: The experiments were carried out in a high-pressure reactor system consisting of a down-flow fixed bed tubular reactor of 100 cm^3 effective volume. The 100 cm^3 tube reactor was working without back-mixing. It contains equipments and devices applied in the reactor system of hydrotreating plants (pumps, separators, heat exchangers, as well as temperature, pressure and gas flow regulators). The operation was mixed phase.

Catalyst: hydrodearomatization experiments were carried out on H-USY zeolite-supported catalyst containing Pt and Pd. The main properties of the support were: SiO_2/Al_2O_3 ratio: 33.5, total- and mesopore surface areas 592.2 m2/g and 51 m^2/g calculated by using BET-plots and t-plots, respectively. The bimetallic Pt-Pd catalyst were prepared by impregnation using $[Pt(NH_3)_4]Cl_2$ and $[Pd(NH_3)_4]Cl_2$. The total amounts of metals was 0.90% (Pd-content: 0.60%, Pt-content: 0.30%), the Pd/Pt mass ratio was 2:1 and the dispersion was 0.51. Pd-, Pt-, Al- and Si-contents were measured by ICP apparatus. Metal dispersion was determined from the amount of chemisorbed CO. After impregnation the catalyst was dried at 70°C, calcined in oxygen stream at 210°C, reduced in-situ in H_2 at 400°C for 12 hours.

Feeds: The feedstocks were real gas oil fractions with different aromatic, sulphur and nitrogen contents. Their important properties are summarized in Table 1.

Process parameters: Hydrodearomatization (HDA) was investigated on the mentioned catalysts in the temperature range of 260 -360°C, total pressures of 35-60 bar, hydrogen to hydrocarbon ratios (H_2/HC thereafter) of 600 Nm^3/m^3 and liquid hourly space velocity (LHSV thereafter) of 1.0-4.0 h^{-1}. The experiments were carried out on catalyst of steady-state activity, by continuous operation.

Methods: The properties of the feeds and products were determined by test methods required by EN 590:2004 standard. The percentile decrease of aromatic content was determined and defined as HDA activity and calculated by the equation 1.

$$\text{HDA, \%} = 100(A_{feed}-A_{product})/A_{feed} \qquad (1)$$

where:

HDA: hydrodearomatization efficiency, %,

A_{feed}: total aromatic content of feed, w%,
$A_{product}$: aromatic content of product, w%.

Table 1. The main characteristics of feeds

Properties	**Feeds**				
	“A”	**“B”**	**“C”**	**“D”**	**“E”**
Density, g/cm^3	0.8370	0.8361	0.8328	0.8607	0.8425
Sulphur content, mg/kg	5	8	119	190	302
Nitrogen content, mg/kg	<1	30	75	158	198
Total aromatic content, %	24.3	32.7	25.7	38.4	32.6
Mono-ring aromatic content, %	21.9	29.5	21.4	26.8	25.4
2+-ring aromatic content, %	2.4	3.2	4.3	11.6	7.2
Boiling range, °C	184-356	167-361	205-363	220-375	210-368

Hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) efficiencies of catalyst were calculated by equations 2 and 3.

$$\text{HDS, \%} = 100(S_{feed}-S_{product})/S_{feed}, \quad (2)$$
$$\text{HDN, \%} = 100(N_{feed}-N_{product})/N_{feed}, \quad (3)$$

where:

HDS: hydrodesulphurization efficiency, %,
HDN: hydrodenitrogenation efficiency, %,
S_{feed}: sulphur content of feed, mg/kg,
$S_{product}$: sulphur content of product, mg/kg,
N_{feed}: nitrogen content of feed, mg/kg,
$N_{product}$: nitrogen content of product, mg/kg.

3. Results and discussion

First the effect of process parameters on gas oil yield and on HDA efficiency was investigated with low sulphur and low nitrogen content feeds (feed “A”, sulphur content: 5 mg/kg, nitrogen content: <1 mg/kg). Figure 1 shows the HDA activity as a function of temperature. Conversion of aromatics increased in the temperature range of 260-330°C, and had a maximum at 330°C (30.1%), and then it decreased with temperature. The thermodynamic equilibrium was probably attained because of lower reaction rates at increasing temperatures after the maximum point, and the thermodynamic equilibrium of the exothermic hydrogenation of aromatics is shifted to dehydrogenation at higher temperatures. Hydrodearomatization efficiency increased with temperature (260-330°C) from about 32.5% to 84% at LHSV of 1.0 h^{-1} and from about 0.7% to 30% at LHSV of 4.0 h^{-1} at $P = 45$ bar. The effect of LHSV and pressure on HDA at 320°C is illustrated in Figure 2. Hydrodearomatization efficiency enhanced with pressure. By raising the pressure from 35 to 60 bar in case of feed “A” the rate of aromatic reduction increased from 69% to 81% at LHSV of 1.0 h^{-1} and at LHSV of 4.0 h^{-1} from 18% to 40%. Hydrodearomatization efficiency improved more significantly with pressure at LHSV of 4.0 h^{-1} (22%) than at LHSV of 1.0 h^{-1} (11%).

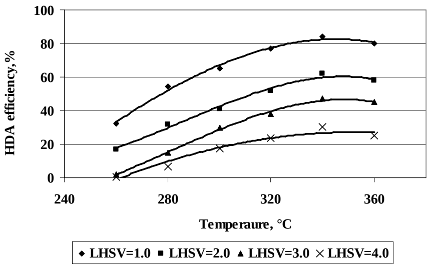

Fig. 1. Effect of temperature and LHSV on HDA activity in case of feed “A” (P=45 bar, H_2/HC = 600 Nm^3/m^3)

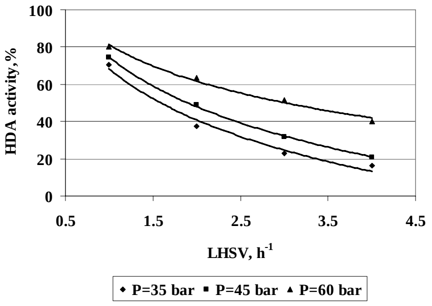

Fig. 2. Effect of LHSV and pressure on HDA activity (T = 320°C, H_2/HC = 600 Nm^3/m^3)

Products of lowest aromatic content could be produced at temperature of 360°C, pressure of 60 bar, LHSV of 1.0 h^{-1} and H_2/HC ratio of 600 Nm^3/m^3 in case of feed “A”. Due to the high hydrodearomatization performance of Pt-Pd/USY catalyst, di- and polycyclic aromatic content of the products was lower than 0.4% even under the mildest process conditions. This value was within the reproducibility of applied test method. Therefore, the change of total aromatic content was nearly the same as that of monoaromatic content.

On the basis of the previous experimental results, hydrotreating of feed containing higher amount of sulphur and nitrogen (Feed “C”, “D” and “E”) was also investigated on Pt-Pd/USY catalysts. The total aromatic content of products was lower than that of the feed at every process parameter applied for both feeds. Fig. 3 shows that HDA activity of the investigated catalyst decreased for feed “C”, “D” and “E” having the highest sulphur and nitrogen content. At 300°C and LHSV= 1.0 h^{-1} the HDA efficiency decreased by only 14% to 53.3% for Pt-Pd/USY catalyst comparing the values obtained with the different feeds under similar process parameters. The reduction of hydrogenating activity may be ascribed not only to the sulphur but to both the sulphur and nitrogen compounds in the feeds, because the partial pressure of produced H_2S increased less than the relative activity decreased (Fig. 3). The hydrodearomatization efficiency for feed “A” (S: 5 mg/kg, N: 1 mg/kg) was similar to that for feed “B” (S: 8 mg/kg, N: 30 mg/kg). The type of acidity of support greatly influences the sulphur and nitrogen tolerance of bimetallic noble metal catalysts, and the Brønsted acidity of the support seems to be high for USY (Varga, 2005, Yoshimura, 2001). It should be noted, however, that the high Brønsted acidity may cause undesired cracking reactions and coke formation. Coke formation significantly lowers reactivity, particularly, in zeolite supports on which pore plugging may become a serious obstacle. From this reason the long term stability of Pt-Pd/USY catalyst (more than 400 hours) is to be tested.

The HDA activity of Pt-Pd/USY catalyst remained relatively high (53.3%) at advantageous process conditions (T = 300°C, P = 45 bar LHSV of 1.0 h^{-1}) in case of feed “E”. This indicates that the applied Pt-Pd/USY catalyst has relatively high sulphur and nitrogen tolerant.

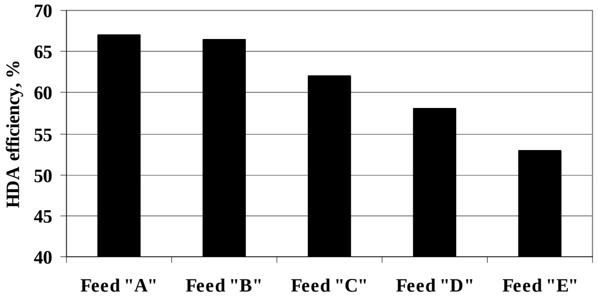

Fig. 3. Effect of sulphur and nitrogen content of feed on HDA efficiency of Pt-Pd/USY catalyst (T = 300°C, P = 45 bar, LHSV = 1.0 h^{-1}, H_2/HC = 600 Nm^3/m^3)

The HDS activity of Pt-Pd/USY catalyst was investigated, too. The change of HDS activity as a function of temperature at different LHSV-s is showed in Fig. 4. The HDS activity considerably increased in the temperature range of 260-320°C, but further increase of the temperature has negligible effect. For example, between 260-280°C the HDS efficiency increased by 11% at LHSV 1.0 h^{-1} to 72% (53 mg/kg sulphur remained), and but between 340-360°C the increase of HDS efficiency was only 2% to 84% (30 mg/kg sulphur remained). Conversion of these refractory sulphur compounds takes mainly place in two steps: first the aromatic ring is hydrogenated then the hydrodesulphurization takes place. Therefore the higher hydrogenation activity results in higher hydrodesulphurization activity. Additionally, the higher acidity of USY zeolite promotes reactions e.g. transalkylation, shift of alkyl groups or dealkylation, etc., resulting in disappearance of alkyl groups from adjacent of sulphur atom (4- or 6-position). This reduces the steric hindrance of the desulphurizing reactions.

As for maximum allowable sulphur content of diesel fuels (50 mg/kg) products having sulphur content lower than 50 mg/kg can be obtained form feed "D" (S: 190 mg/kg) at a temperature of 300°C, pressure of 45 bar and LHSV = 1.0 h^{-1} or at 280°C, pressure of 60 bar and LHSV = 2.0 h^{-1} using Pt-Pd/USY catalyst.

The change of HDN efficiency of catalysts as function of temperature and LHSV at P = 45 bar are displayed in Fig. 5.

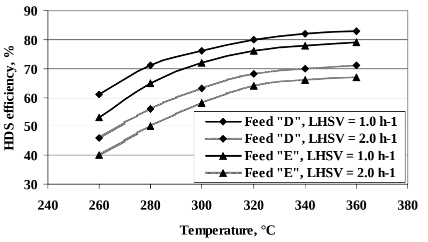

Fig. 4. Effect of temperature and LHSV on HDS efficiency of catalysts (P = 45 bar, Feed „D" and „E")

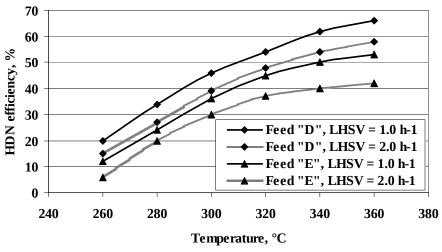

Fig. 5. Effect of temperature and LHSV on HDN efficiency of catalysts (P = 45 bar, Feed „D" and „E")

This shows that HDN efficiency of Pt-Pd/USY catalyst was always considerably lower than the HDS efficiency. It varied between 5-65% in function of process parameters. Compared to the HDS efficiency the HDN efficiency also increased in the temperature range of 260-320°C, but further increase of the temperature has negligible effect in case of higher LHSV (2.0 h^{-1}).

4. Conclusion

Effect of the sulphur content of the gas oil feeds (up to 302 mg/kg sulphur) on the hydrodearomatizing activity of Pt(0.3%)-Pd(0.6%)/USY and the impact of process parameters (temperature, pressure, LHSV) on the hydrodearomatization, hydrodesulphurization and hydrodenitrogenation efficiency was studied. Applying the feed having the lowest sulphur (5 mg/kg) and nitrogen (1 mg/kg) contents HDA activity of the catalyst changed between 5-85% in function of process parameters. It increased with temperature, pressure and decreased with LHSV. The results of experiments obtained under various conditions showed that the use of practically sulphur and nitrogen-free feed provided relatively high HDA activities. Applying gas oils of higher sulphur and nitrogen content resulted in decrease of HDA activities. Pd-Pt/USY provides high sulphur tolerance because its hydrodearomatization activity decreased by only 25% in case of feed “E” with high sulphur (302 mg/kg) and nitrogen (198 mg/kg) content. The hydrodesulphurization efficiency changed from 40% to 85% and the hydrodenitrogenation efficiency changed between 5-65% affected by the applied process parameters.

Summing up the results, the investigated catalyst (Pt-Pd/USY) provided high HDA, HDS and HDN activities in presence of sulphur and nitrogen in feed. That’s why high sulphur (up to 300 mg/kg) and nitrogen (up to 200 mg/kg) content can be upgraded to high quality (low sulphur, nitrogen and aromatic content) blendstocks for diesel fuel in the hydrodearomatization pressure range (45-60 bar) in one step.

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