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Investigation of hydrodearomatization of gas oils on noble metal/support catalysts

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ABSTRACT

Due to the more and stricter requirements of diesel fuels, one of the most important key factors of production of modern diesel fuel blending components is the two-stage deep hydrodesulphurization and hydrodearomatization, where in the second step noble metal catalysts are used for the deep hydrodearomatization of prehydrogenated feeds. In this paper, the results of hydrodearomatization of different sulphur- and nitrogen containing real gas oil fractions on PtPd/USY zeolite, PtPd/amorphous SiO_2–Al_2O_3 and PtPd/γ–Al_2O_3 catalysts are presented. In case of PtPd/USY catalyst, the effect of Pd/Pt atomic ratio on the sulphur tolerance was also investigated, additionally, the effect of sulphur and nitrogen content of the feeds and the process conditions on HDA, HDN and HDS activities were studied. The main goal of our experiments was to find a bimetallic PtPd/USY catalyst possessing Pd/Pt mass ratio of 2:1 (Pd/Pt atomic ratio of 3.7:1), which was suitable for the deep hydrodearomatization of relatively high sulphur (up to 300 mg S/kg) and nitrogen (up to 200 mg N/kg) containing feeds. In case of optimal process parameters ($T = 310\,^{\circ}C$, $P = 60$ bar, LHSV = 1.0–1.5 h^{-1}, H_2/hydrocarbon volume ratio = 600 N m^3/m^3), low total aromatic (<10%), practically sulphur and nitrogen free products (≤10 mg S/kg and ≤1 mg N/kg) having high cetane number (56–58) could be produced, which are less pollutant diesel fuel blending components. The relatively high activity for hydrodesulphurization and hydrodearomatization, and the low hydrocracking activity of this catalyst provides flexibility for the two-step deep hydrodesulphurization and deep hydrodearomatization processes. It means that applying this catalyst, the deep hydrodearomatization and further deep heteroatom removal of different feeds can be performed with high gas oil yield. Therefore, it is not necessary to apply deep hydrodesulphurization to max. 50 or 10 mg S/kg in the first stage on transition metal/support catalysts.

1. Introduction

The sulphur content of diesel fuels has been reduced worldwide (e.g., in EU from 2005: <50 (<10) mg/kg and <10 mg/kg from 2009) [1]. In addition the polycyclic aromatic content will be also limited (about 2–4% from 2009) and the total aromatic content is expectedly desired to be below 15–20% in the near future. Reduction of the aromatic content of diesel fuels is also relevant, because aromatic hydrocarbons possess low cetane numbers, and they contribute to the increase of vehicle HC (hydrocarbon) and PM (particulate matter) emissions as well. The NO_X emission is also increased by the higher temperature combustion of aromatic compounds. The nitrogen containing compounds in the diesel fuel are also important, because—beside the reaction between N_2 and O_2—their combustion enhance the NO_X-emission of diesel-fuelled vehicles. To achieve lower levels of sulphur and aromatics in diesel fuels, an integrated two-stage deep hydrotreating experimental plant was set up. In this plant, conventional $NiMo/Al_2O_3$ or $CoMo/Al_2O_3$ sulphide catalysts were used in the first stage of deep hydrodesulphurization and partial hydrodearomatization, then sulphur-tolerant noble metal catalysts were used in the second stage for deep hydrodearomatization and further deep hydrodesulphurization [2]. Therefore in recent years, sulphur and nitrogen tolerant (up to 50–200 mg/kg) precious metal catalysts have attracted much attention for the hydrogenation of aromatics in diesel fuels [3], too. In case of monometallic noble metal catalysts (e.g. Pt/support or Pd/support), the sulphur content in the feedstock must be strictly reduced (≤10 mg/kg) before the catalyst contacts with the feedstock due to its low sulphur tolerance. Bimetallic catalysts (e.g. PtPd/USY, PtPd/HDAY, PtPd/γ–Al_2O_3, PtPd/MCM-41, PtPd/amorphous SiO_2–Al_2O_3, PtPd/ZrO_2) and/or appropriate acidic support can be used to enhance the sulphur tolerance [4,5]. How-

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ever, sulphur tolerance of the bimetallic catalysts was influenced by numerous factors, such as preparation methods [4,6], degree of Pt–Pd alloy formation, Pt–Pd particle sizes [7] and interactions between the Pt–Pd particles and acidic support [4,8,9]. In the literature, there are a few publications about sulphur and nitrogen tolerance of noble metal catalysts in case of real gas oils as feeds.

The main objective of our research work was to find a noble metal/support catalyst which is suitable for the hydrodearomatization of high sulphur- and nitrogen containing gas oils. In our experiments, the effect of sulphur- and nitrogen content of feeds on the HDA, HDN and HDS activities of the catalysts were studied. First three catalysts were investigated, which were the following: Pt(0.3%)Pd(0.6%)/USY zeolite, Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 and Pt(0.3%)Pd(0.6%)/γ–Al_2O_3. Finally in case of PtPd/USY zeolite, the effect of Pd/Pt atomic ratio on sulphur tolerance was also investigated. The main goal of our experiments was to find a PtPd/support catalyst which is suitable for deep hydrodearomatization and further deep hydrodesulphurization of gas oils (prehydrogenated in first step of two-stage hydrogenation process) containing up to 300 mg S/kg sulphur and up to 200 mg N/kg nitrogen in second step of two-stage deep gas oil hydrogenation process.

2. Experimental

2.1. 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, which operated without back-mixing [1]. The reactor system contained such equipment and devices, which are applied in the reactor system of a hydrotreating plant (Fig. 1).

Table 1
Standard test methods applied for characterization of feeds and products.

Properties	Standard test methods	
	EU	USA
Density	EN ISO 3675	ASTM D1298
Sulphur content	EN ISO 20846	ASTM D2622
Nitrogen content	ASTM D 6366	ASTM D 6366
Aromatic content	EN 12916	ASTM D 1319
Distillation properties	EN ISO 3405	ASTM D 86
Cetane number	EN ISO 5165	ASTM D 613

2.2. Methods

The properties of the feeds and products were determined by standard test methods required by EN and ASTM standards (Table 1). The Pd-, Pt-, Al- and Si-content of catalysts was measured by ICP apparatus. The surface area was calculated by BET-plots and *t*-plots. Metal dispersion was determined from the amount of chemisorbed CO at 50 °C. The acidity was determined by temperature programmed desorption of NH_3 (TPD). In this procedure, 55 mg of catalyst in a quartz tube reactor was prepared and heated up to 400 °C with He flow. After cooling to 150 °C, the samples were saturated by ammonia, then heated linearly to 650 °C at a rate of 15 °C/min. The desorbed ammonia was absorbed from the tail gas with HCl, which was titrated afterwards. The percentile decrease of aromatic content was determined and defined as HDA activity and calculated by Eq. (1). Hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) activities of the catalysts were calculated by Eqs. (2) and (3).

$$\mathrm{HDA}\,(\%) = \frac{100(A_{\mathrm{feed}} - A_{\mathrm{product}})}{A_{\mathrm{feed}}} \tag{1}$$

$$\mathrm{HDS}\,(\%) = \frac{100(S_{\mathrm{feed}} - S_{\mathrm{product}})}{S_{\mathrm{feed}}} \tag{2}$$

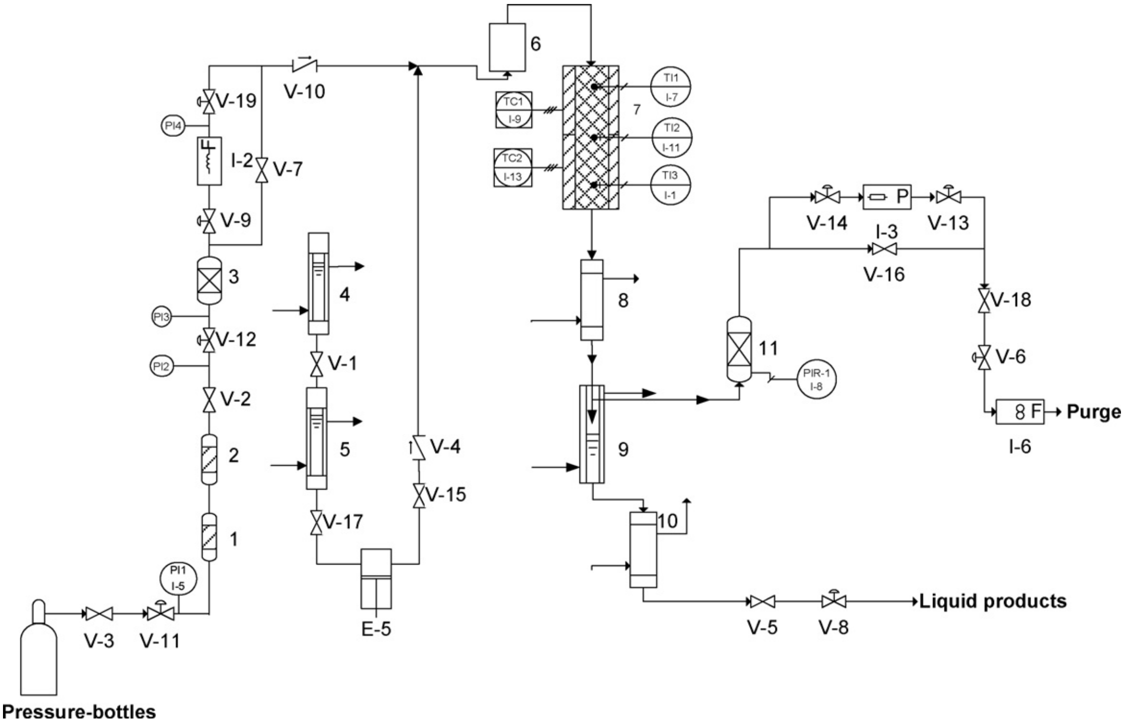


Fig. 1. High-pressure reactor system (cut-off valves: V-1, V-3, V-7, V-8, V-9, V-10, V-15, V-16, V-18; control valves: V-2, V-4, V-5, V-6, V-13, V-14, V-17, V-19; V-20; manometers: PI1, PI2, PI3, PI4; oxygen converter: 1; gas dryer: 2; gas filters: 3, 11; gas flow meter/controller: FIC-1; back-pressure valves: V-11, V-12; storage burette: 4; feeder burette: 5; pump: P-1; pre-heater: 6; reactor: 7; coolers: 8,10; separator: 9; pressure register: PIR-1; wet gas meter: FI-1; pressure meter/controller: PIC-1).

Table 2
The total metal contents and Pd/Pt ratios of the PtPd/USY catalysts.

Properties	PtPd/USY catalyst with different Pd/Pt atomic ratio				
	I	II	III	IV	V
Pd/Pt mass ratio	6:1	4:1	2:1	1:1	1:3
Pd/Pt atomic ratio	12.5:1	7.4:1	3.7:1	1.6:1	0.6:1
Pd content (%)	0.80	0.72	0.60	0.45	0.23
Pt content (%)	0.13	0.18	0.31	0.46	0.69
Total metal content (%)	0.93	0.90	0.91	0.91	0.92
Dispersion	0.55	0.51	0.48	0.43	0.41

$$\mathrm{HDN}\,(\%) = \frac{100(N_{\mathrm{feed}} - N_{\mathrm{product}})}{N_{\mathrm{feed}}} \qquad (3)$$

where: HDA: hydrodearomatization efficiency, %; A_{feed}: total aromatic content of feed, w%; A_{product}: total aromatic content of product, w%; HDS: hydrodesulphurization efficiency, %; HDN: hydrodenitrogenation efficiency, %; S_{feed}: sulphur content of feed, mg S/kg; S_{product}: sulphur content of product, mg S/kg; N_{feed}: nitrogen content of feed, mg N/kg; N_{product}: nitrogen content of product, mg N/kg.

2.3. Catalysts

The investigated catalysts [10] were PtPd/USY zeolite (SiO_2/Al_2O_3 overall molar ratio: 33.5, total- and mesopore surface areas 650 m^2/g and 51 m^2/g, total metal content: 0.9%, Pd/Pt mass ratio: 6:1 to 1:3, dispersion: 0.41–0.55, acidity: 0.20 mmol/g) catalysts possessing various metal contents and Pd/Pt ratios, which are summarized in Table 2. As reference catalysts, bimetallic PtPd/amorphous SiO_2–Al_2O_3 (platinum-content: 0.3%, palladium-content: 0.6%, Al_2O_3 content: 15%, surface area: 292 m^2/g, dispersion: 0.41, acidity: 0.18 mmol/g) and PtPd/γ-Al_2O_3 (platinum-content: 0.3%, palladium-content: 0.6%, surface area: 182 m^2/g, dispersion: 0.35, acidity: 0.12 mmol/g) were used.

2.4. Feeds

The feedstocks were prehydrogenated real gas oil fractions with different aromatic, sulphur and nitrogen contents from Hungarian and Russian crudes. Their major properties are summarized in Table 3.

2.5. Process parameters

Hydrodearomatization (HDA) was investigated under the following process parameters: temperature range: 260–360 °C, total pressure: 35–80 bar, hydrogen to hydrocarbon ratios (H_2/HC thereafter): 200–1000 Nm^3/m^3 and liquid hourly space velocity (thereafter LHSV): 0.75–4.0 h^{-1}. The experiments were carried out on catalysts of steady-state activity, in continuous operation.

3. Results and discussion

Our experimental work was divided up to two main segments. First, the suitable catalyst was chosen for deep hydrodearomatization of relatively high sulphur but low nitrogen containing feeds ("A", "B" and "C") among the investigated Pt(0.3%)Pd(0.6%)/USY zeolite, Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 and Pt(0.3%)Pd(0.6%)/γ–Al_2O_3 catalysts. Based on these results, the activities and sulphur tolerance of these catalysts were compared. Finally, the hydrodearomatization activity for aromatic saturation, desulphurization and denitrogenation of high sulphur and high nitrogen containing feeds (feed "D, "E" and "F") was studied on the most suitable PtPd/USY zeolite catalysts. In this section, the effect of Pd/Pt atomic ratio of catalyst on the HDA, HDS and HDN activities and on the heteroatom tolerance were also studied. By these experiments, the enhancement of sulphur- and nitrogen tolerance of PtPd/USY zeolite catalyst were determined.

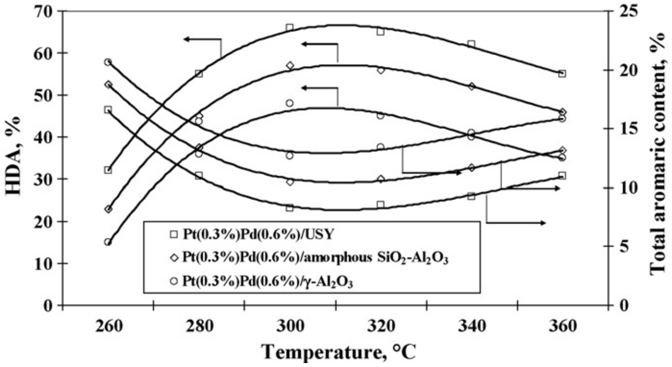


Fig. 2. Effect of the temperature on the HDA activity of investigated catalysts (feed "A", P = 45 bar; LHSV: 1.0 h^{-1}, H_2/HC: 600 Nm^3/m^3).

First, the HDA activities of Pt(0.3%)Pd(0.6%)/USY, Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 and Pt(0.3%)Pd(0.6%)/γ-Al_2O_3 catalysts were investigated in case of feeds having different sulphur content ("A", "B" and "C"). The results are displayed in the function of temperature in Fig. 2, where feed "A" has the lowest sulphur and nitrogen content. Shape of the curves shows that the highest HDA activity was attained at 310 °C (total aromatic content: 8.3% on Pt(0.3%)Pd(0.6%)/USY catalyst). Exceeding this temperature, the reduction of aromatics begun to decrease. Certainly, the thermodynamic equilibrium was attained at 310 °C, thereafter the equilibrium of the exothermic hydrogenation of aromatics is shifted toward dehydrogenation. Applying the feed "A", the HDA activity of the Pt(0.3%)Pd(0.6%)/USY catalyst varied between 5-85% (total aromatic content was between 4.0 and 16.5%, Cetane number [thereafter: CN] was between 57 and 54). In the investigated LHSV range (0.75–4.0 h^{-1}), the HDA activity decreased by increasing LHSV from 72% to 52% (the rest of total aromatic content increased from 7.6% to 12.1%, CN decreased from 58 to 55) in case of Pt(0.3%)Pd(0.6%)/USY, from 62% to 41% (the total aromatic content of products increased from 10.5% to 14.1%, CN decreased from 57 to 54) applying Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 and from 51% to 37% (total aromatic content increased from 12.1% to 16.3%, CN decreased from 55 to 53) on Pt(0.3%)Pd(0.6%)/γ-Al_2O_3 catalyst at 320 °C and 45 bar (Fig. 3). The effect of pressure and H_2/HC volume ratio were also investigated in the range of 35–80 bar and 200–1000 $N\,m^3/m^3$. The HDA activity increased with the pressure and the H_2/HC volume ratio on all investigated catalysts. H_2/HC volume ratio had the lowest effect on the HDA activity in the

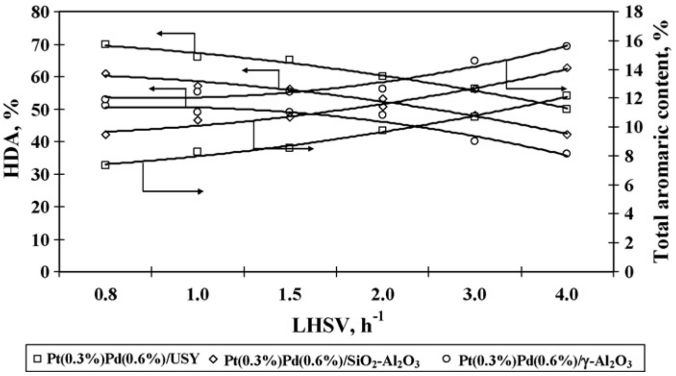


Fig. 3. Effect of the LHSV on the HDA activity of the investigated catalysts (feed "A", P = 45 bar; T = 320 °C, H_2/HC: 600 Nm^3/m^3).

Table 3
The main properties of feeds.

Properties	Feeds					
	A	B	C	D	E	F
Density at 15.6 °C (g/cm^3)	837.0	836.1	832.8	860.7	842.5	849.8
Sulphur content (mg S/kg)	5	152	280	190	302	320
Nitrogen content (mg N/kg)	<1	8	14	58	153	203
Total aromatic content (%)	24.3	32.7	25.7	38.4	32.6	34.5
Mono-ring aromatic (%)	21.9	29.5	21.4	26.8	25.4	26.4
2+-ring aromatic content (%)	2.4	3.2	4.3	11.6	7.2	8.1
Cetane number (*CN*)	50	50	49	48	47	47
Boiling range (°C)	184–356	167–361	205–363	220–375	210–368	212–367

investigated H_2/HC volume ratio range. The reason for this slight decrease was probably due to the fact, that the enhancement of the partial pressure of hydrogen not only facilitated the aromatic saturation reactions but slightly depressed the diffusion of the aromatics onto the catalytic active centres by the dilution of the reaction mixture. According to this, our experiments were carried out by 600 N m^3/m^3 H_2/HC volumetric ratio, which was previously found optimal by us. The HDA activity strongly depended on the total pressure (Fig. 4). On increasing the total pressure from 35 to 80 bar, the HDA activity increased by about absolute 35% on Pt(0.3%)Pd(0.6%)/USY catalysts. The CN of the products increased with decreasing aromatic content. The highest value was 58 (feed CN: 50), produced on Pt(0.3%)Pd(0.6%)/USY catalyst at 320 °C, 45 bar and LHSV = 1.0 h^{-1}.

As it can be seen, the HDA activity of the catalysts decreased in the following order: Pt(0.3%)Pd(0.6%)/USY > Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 > Pt(0.3%)Pd(0.6%)/γ-Al_2O_3. The higher aromatic conversion on Pt(0.3%)Pd(0.6%)/USY and Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 catalysts should be attributed to the higher acidity of these supports ensuring higher and more uniform metal dispersion enabling stronger adsorption of aromatics [1,2], than in the case of Pt(0.3%)Pd(0.6%)/γ–Al_2O_3. However, there was considerable difference between the surface areas of Pt(0.3%)Pd(0.6%)/USY and Pt(0.3%)Pd(0.6%)/amorphous $SiO_2Al_2O_3$ catalysts (650 m^2/g and 292 m^2/g) but the difference between their HDA activities was found to be only 10-15% under similar process conditions. In addition, the acidity of USY is higher than that of amorphous silica–alumina, thus the adsorption of aromatics on this catalyst support is higher [1–3].

The hydrodesulphurization (HDS) activity of the catalysts was also investigated. The change of HDS activity as a function of temperature is shown in Fig. 5 in case of feed “C” (sulphur content: 280 mg S/kg, nitrogen content: 14 mg N/kg).

Using Pt(0.3%)Pd(0.6%)/USY catalyst the HDS activity considerably increased in the temperature range of 260–320 °C, but further increase of the temperature has negligible effect. The attainable sulphur content reduction was always remarkably lower on Pt(0.3%)Pd(0.6%)/$SiO_2Al_2O_3$ catalyst. For example, at 320 °C and LHSV 1.0 h^{-1}, the HDS activity of Pt(0.3%)Pd(0.6%)/USY was 81.0% (product sulphur content: 53 mg S/kg) while that value was 43.0% (product sulphur content: 159 mg S/kg) for Pt(0.3%)Pd(0.6%)/SiO_2–Al_2O_3. The effect of the temperature on the sulphur content of products and on the hydrodesulphurization activity is summarized in the following. It seems probable that sulphur compounds remaining in the gas oil after the previous hydrodesulphurization should be polynuclear heterocyclic compounds like dibenzothiophenes having one or more alkyl groups in the vicinity of the sulphur atom (e.g. 4,6-dimethyldibenzothiophene). In these compounds, the alkyl groups block the bonding of the sulphur atom to the catalytic active centres, thus the direct desulphurization is blocked sterically. Hence, the conversion of the sulphur containing heterocyclic compounds takes place via a reaction pathway, where the first step is the saturation of either aromatic ring of the alkyl dibenzotiophene molecule. Then, due to the enhanced flexibility of the arisen cyclohexyl ring, the alkyl group could take such position, where its steric blocking effect on the splitting of C-S bond is decreased. The conversion via the partial saturation of the aromatic system can be seen in Fig. 6 [11,12]. Therefore, the higher aromatic hydrogenation activity results in higher hydrodesulphurization activity. Additionally, the higher acidity of USY zeolite comparing to the amorphous SiO_2–Al_2O_3 or γ-Al_2O_3 promotes reactions, e.g., transalkylation, positional isomerization of alkyl groups or dealkylation, etc., resulting in migration of alkyl groups from adjacent sulphur atom (4- or 6-position). This also reduces the steric hindrance of the desulphurization reactions and increases the HDS activity [16].

The Pt(0.3%)Pd(0.6%)/γ-Al_2O_3 catalyst had the lowest HDS (8–23%, sulphur content of products changed between 257 and 210 mg S/kg) activity attributed to the lowest acidity of the catalyst support. Products of maximum allowable sulphur content for diesel fuels (50 mg/kg) could be obtained from feed “C” at

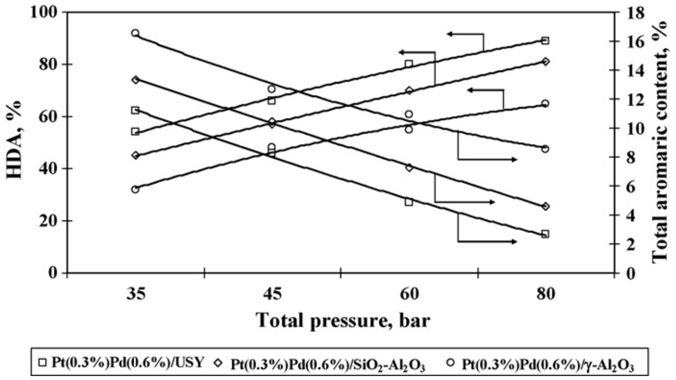


Fig. 4. Effect of total pressure on the HDA activity of the investigated catalysts (feed “A”, H_2/HC: 600 Nm^3/m^3; *T* = 320 °C, LHSV = 1.0 h^{-1}).

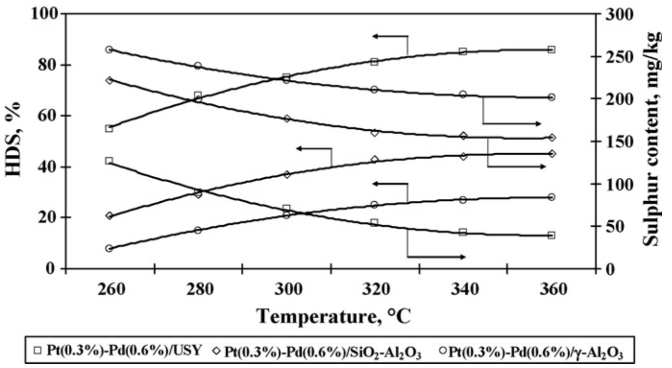


Fig. 5. Effect of temperature on the HDS activity of the investigated catalysts (feed “C”, *P* = 45 bar (a); *P* = 60 bar (b); LHSV: 1.0 h^{-1}, H_2/HC: 600 Nm^3/m^3).

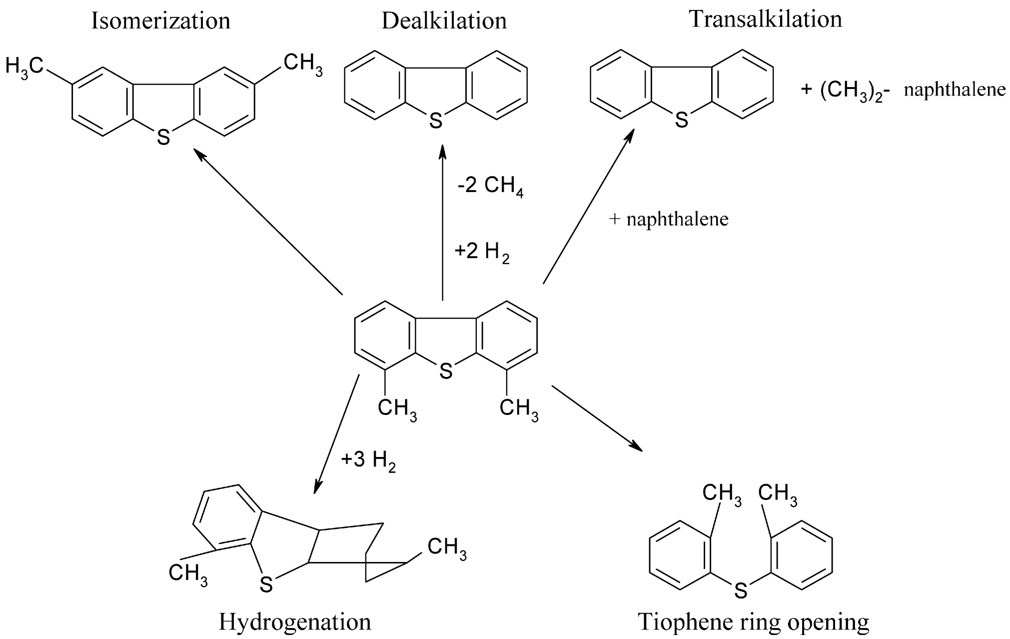


Fig. 6. Alternative reaction ways for the desulphurization of sterically hindered dialkyl-dibenzotiophene.

600 N m^3/m^3 H_2/HC ratio, 320 °C temperature, 45 bar pressure and 1.0 h^{-1} LHSV or at 300 °C, 60 bar pressure and 1.0 h^{-1} LHSV using Pt(0.3%)Pd(0.6%)/USY catalyst. Products containing less than 10 mg S/kg sulphur can be obtained at 340 °C and 60 bar. From feed “C” a product containing maximum 50 mg/kg sulphur could not be obtained by the application of Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 or Pt(0.3%)Pd(0.6%)/γ-Al_2O_3 catalyst.

The effect of sulphur on the HDA activity of catalysts was tested using feed “B” and “C”. The experiments were carried out at 320 °C, 45 bar pressure and 600 N m^3/m^3 H_2/HC volume ratio. HDA activities of catalysts for different feeds are shown in Fig. 7. The lowest decrease of hydrodearomatization activity by the sulphur content of feed was observed on Pt(0.3%)Pd(0.6%)/USY, somewhat higher on Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 and very high on Pt(0.3%)Pd(0.6%)/γ-Al_2O_3. The reduction of hydrogenating activity could be ascribed to the sulphur compounds in the feed and the H_2S produced from hydrodesulphurization reactions [1,2]. The result suggests that the acidity of support greatly influences the sulphur tolerance of bimetallic noble metal catalysts, and the Brønsted acidity of the support seems to be decisive being higher for USY than for silica-alumina and for γ-alumina [2]. It should be noted, however, that the high Brønsted acidity may cause undesired cracking reactions and coke formation, which significantly reduces the activity of zeolite supports.

Product possessing the highest cetane number (59) could be produced at high HDA (maximum HDA efficiency was at 320 °C) activity in case of feed “A” on Pt(0.3%)Pd(0.6%)/USY catalyst (P = 80 bar, LHSV = 0.75 h^{-1}, H_2/HC volume ratio: 1000 N m^3/m^3).

The reversibility of the effect of sulphur on the hydrodearomatization activity was also studied using feed “A” (5 mg S/kg) and “B” containing 158 mg S/kg sulphur (Fig. 8.). These experiments were carried out at 300 °C, 2.0 h^{-1} LHSV, 45 bar and 600 Nm^3/m^3 H_2/HC volume ratio. The lowest degree of activity loss was observed on Pt(0.3%)Pd(0.6%)/USY, and somewhat higher on Pt(0.3%)Pd(0.6%)/amorphous SiO_2-Al_2O_3. In case of Pt(0.3%)Pd(0.6%)/γ-Al_2O_3 catalyst, the loss of hydrodearomatization activity was almost 90% after the switch to higher sulphur containing feed “B”. After 15 h, the

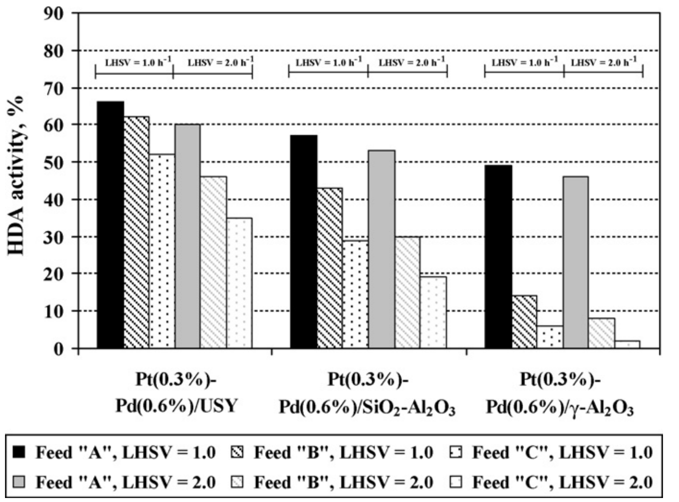


Fig. 7. Effect of feed on the HDA activity of the investigated catalysts (feeds “A”, “B” and “C”, P = 45 bar; LHSV = 1.0–2.0 h^{-1}, T = 320 °C, H_2/HC: 600 Nm^3/m^3).

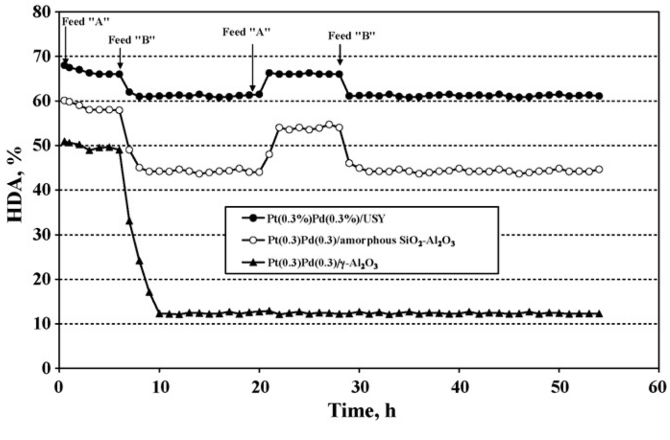


Fig. 8. Activity test of catalysts applying high (feed “B”) and low sulphur (feed “A”) gas oils (T = 300 °C; LHSV = 2.0 h^{-1}; P = 45 bar; H_2/HC = 600 Nm^3/m^3, sulphur content of feeds: “A”, 5 mg/kg, “B”, 152 mg/kg).

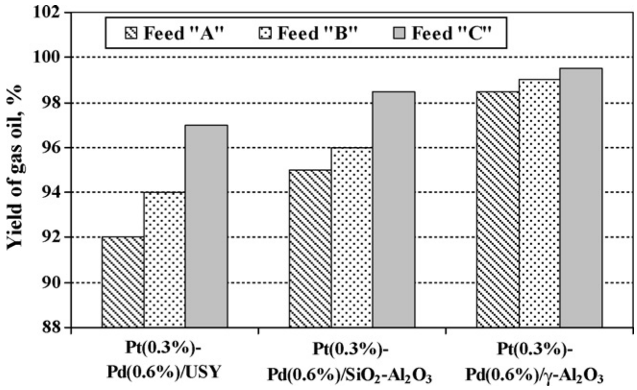


Fig. 9. Effect of feed on the gas oil yield (feed "A", "B" and "C", $P = 45$ bar; LHSV = 1.0 h^{-1}, $T = 320$ °C, H_2/HC: 600 Nm^3/m^3).

feeding was switched back to the practically sulphur free "A" feed. Then the activity of Pt(0.3%)Pd(0.6%)/USY was regained, that of Pt(0.3%)Pd(0.6%)/amorphous SiO_2-Al_2O_3 was partially regained, but the initial activity was not recovered. The hydrodearomatization activity of Pt(0.3%)Pd(0.6%)/USY and Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 catalysts was decreased to the previous value after the replicated change of feeds from "A" to "B". These effects indicate that there were two types of sulphur poison: one resulting in reversible and the other in irreversible activity decrease. The reversible poisoning can presumably be attributed to competing adsorption of H_2S and the aromatic compounds on the active sites decreasing the rate of hydrodearomatization. Different proposals were published for the explanation of irreversible sulphur poisoning, e.g. the poisoning of active metals by sulphur or decrease of dispersion of active metals by agglomeration accelerated by sulphur species and H_2S [13–15]. The HDA activity of Pt(0.3%)Pd(0.6%) γ-Al_2O_3 catalyst was, however, not recovered indicating irreversible poisoning by sulphur presumably because of formation of surface sulphides.

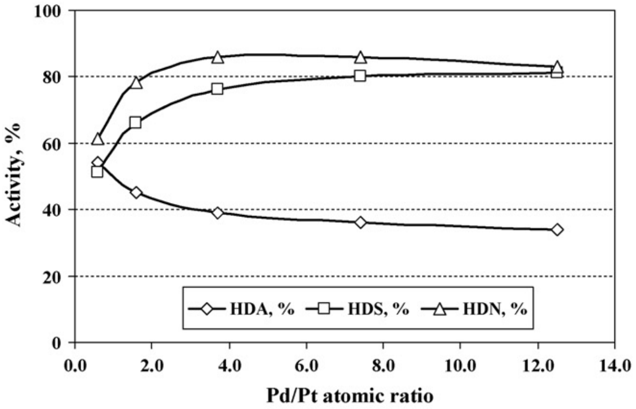
The comparison of the hydrocracking activity of the investigated catalysts was based on the product yield, which was also studied as a function of process parameters. The products were distillated to a lower (boiling range: <200 °C) and a higher (boiling range: >200 °C) fraction. The latter was the gas oil (target) product.

The yield of gas oil was between 97 and 83% on Pt(0.3%)Pd(0.6%)/USY, between 98.5 and 87.0% on Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3 and between 99 and 93% on Pt(0.3%)Pd(0.6%)/γ-Al_2O_3 catalyst in the range of investigated process parameters (Fig. 9).

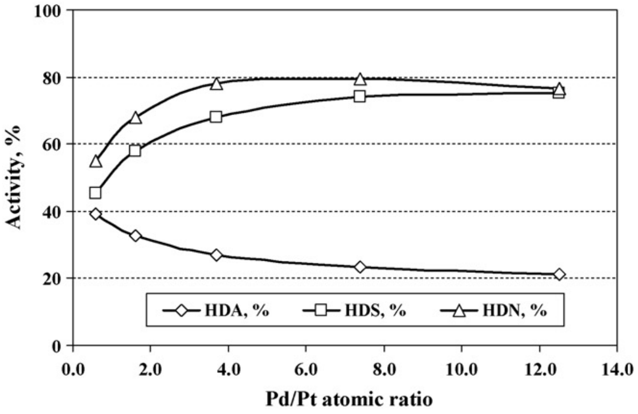
It was concluded, that the hydrocracking activity of the investigated catalysts depended strongly on the properties of the feeds (mainly the heteroatom-sulphur and nitrogen-content), because the heteroatom content in the feeds (mainly the nitrogen content) greatly influences the acidity of the support. The relatively high hydrodesulphurization and hydrodearomatization activity and the low hydrocracking activity provides the flexibility of two step deep hydrodesulphurization and deep hydrodearomatization processes applying Pt(0.3%)Pd(0.6%)/USY catalyst. This means that by applying this catalyst hydrodearomatization and hydrodesulphurization of different feeds having relatively high sulphur and nitrogen contents can be performed with high gas oil yield. Therefore it is not necessary to apply deep hydrodesulphurization to 50 or 10 mg S/kg in the first stage on transition metal/support catalysts.

Based on our results, the HDA activity and the sulphur tolerance of the investigated catalysts decreased in the following order: Pt(0.3%)Pd(0.6%)/USY zeolite> Pt(0.3%)Pd(0.6%)/amorphous SiO_2–Al_2O_3> Pt(0.3%)Pd(0.6%)/γ-Al_2O_3. These results indicate, that Pt(0.3%)Pd(0.6%)/USY was advantageously applicable for deep hyrodearomatization and further deep hydrodesulphurization of relatively high sulphur containing feeds with high gas oil yield in the second step of two stage deep hydrodesulphurization and deep hydrodearomatization processes.

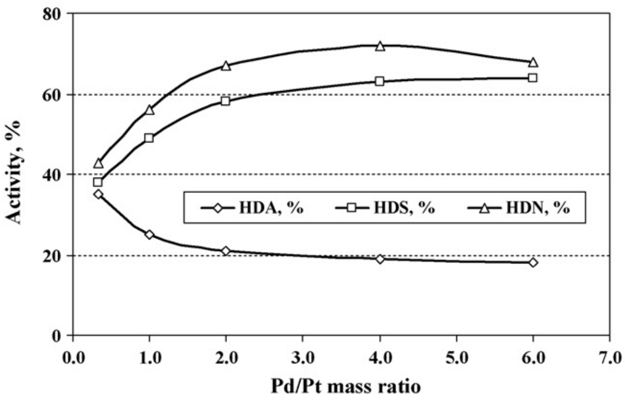
Beside the effect of catalyst support, the effect of ratio of noble metals on the activity of USY zeolite was investigated as well. The influence of Pd/Pt mass ratio on the HDA, HDN and HDS activities in case of feed "D" is shown in Fig. 10a ($T = 320$ °C, $P = 45$ bar; LHSV: 1.0 h^{-1}, H_2/HC: 600 N m^3/m^3). The conversion of total aromatics decreased from about 54% to 34% as the Pd/Pt mass ratio increased from 0.6 to 12.5. Presumably, the saturation of aromatic compounds, mainly that of mono aromatics require higher hydrogenation activity, which is provided by the platinum metal. As it



a, (Feed D)



b, (Feed E)



c, (Feed F)

Fig. 10. Effect of Pd/Pt atomic ratio on the HDA, HDS and HDN activities of PtPd/USY catalysts ($T = 320$ °C, $P = 45$ bar; LHSV: 1.0 h^{-1}, H_2/HC: 600 Nm^3/m^3).

Table 4
The advantageous process conditions for production of practically sulphur and nitrogen free, low total aromatic containing products on PtPd (Pd/Pt atomic ratio: 3.7:1)/USY catalyst (H_2/CH = 600 Nm^3/m^3).

Process parameters	Feeds					
	A	B	C	D	E	F
Temperature (°C)	320	320	340	340	340	360
Pressure (bar)	45	45	60	45	60	60
LHSV (h^{-1})	2.0	2.0	1.0	1.0	1.0	1.0
Products						
Yield (%)	89	92	88	92	93	94
Density, 15 °C (kg/m^3)	823.5	835.7	845.3	840.7	855.8	859.2
Sulphur content (mg S/kg)	<1	9	9	35	39	45
Nitrogen content (mg N/kg)	<1	<1	<1	3	11	28
Total aromatic content (%)	8.3	10.3	12.4	14.8	16.4	17.8
Cetane number	58	57	57	56	55	55

can be seen, the conversion of sulphur compounds monotonously increased from about 51% to 81% with increasing Pd/Pt ratio. Meanwhile, the conversion of nitrogen compounds increased with the Pd/Pt ratio in the beginning, then–after reaching a maximum (86%) at Pd/Pt mass ratio 2:1 (Pd/Pt atomic ratio 3.7:1)—it slightly began to decrease. Based on the experimental results, it could be assessed that the maximum of the HDS and HDN activities did not coincide. Experiments carried out with feed “E” provided similar results (Fig. 10b). The explanation of the different change of HDS and HDN activities requires further investigations.

The lowest HDA (18–35%), HDS (38–63%) and HDN (42–73%) efficiencies were obtained on feed “F” with up to 320 mg S/kg sulphur and 203 mg N/kg nitrogen content (Fig. 10c). Beside the tolerance of sulphur compounds, the one of nitrogen is also an important issue because most petroleum feedstock contain basic (pyridine, quinoline, acridine) and non-basic (pyrole, indole, carbazole) nitrogen compounds, which are strongly adsorbed on the acidic sites of the catalyst support. This phenomena reduces the electron-deficiency of noble metals, thus suppresses the sulphur tolerance and HDA activity of catalysts [2]. Based on the results with high nitrogen containing feed “D”, “E” and “F”, the catalyst having Pd/Pt mass ratio of 2:1 (Pd/Pt atomic ratio: 3.7:1) showed the best performance.

PtPd(Pd/Pt atomic ratio: 3.7:1)/USY could be applied for hydrodearomatization, hydrodesulphurization and hydrodenitrogenation of up to 300 mg S/kg sulphur and up to 200 mg N/kg nitrogen containing feed in the second step of two stage processes. The advantageous process conditions were summarized in Table 4, where $\leq$15% total and $\leq$2% polycyclic aromatic containing, maximum 50(10) mg S/kg sulphur and maximum 10 mg N/kg nitrogen containing products were produced on this catalyst with relatively high gas oil yield. It can be seen, that in case of the highest sulphur- and nitrogen containing feed “E” and “F” deep HDS, HDN and HDA could also be performed on PtPd(Pd/Pt atomic ratio: 3.7:1)/USY catalysts, but at relatively higher temperature (340 or 360 °C).

According to our results, a bimetallic PtPd/USY catalyst possessing Pd/Pt atomic ratio of 3.7:1 (Pd/Pt atomic ratio of 2:1) was found to be favourable for deep hydrodearomatization, hydrodesulphurization and hydrodenitrogenation of relatively high sulphur (up to 300 mg S/kg) and nitrogen (up to 200 mg N/kg) containing feed. In case of optimal process parameters (T = 310 °C, P = 60 bar, LHSV = 1.0–1.5 h^{-1}, H_2/hydrocarbon volume ratio = 600 N m^3/m^3), low aromatic (<10%), practically sulphur and nitrogen free products ($\leq$10 mg S/kg and $\leq$1 mg N/kg) having high cetane number (54–58) could be produced which are less pollutant diesel fuel blending components.

4. Conclusion

The objective of our study was to find a noble metal/support catalyst, which is suitable for the deep hydrodearomatization of high sulphur and nitrogen containing gas oils. Additionally, the effect of Pd/Pt atomic ratio on the HDA, HDS and HDN activities was also investigated.

The HDA activity of the catalysts decreased in the order PtPd/USY > PtPd/SiO_2-Al_2O_3 > PtPd/γ-Al_2O_3, which attributed to the higher acidity of their supports. The HDS activity of the catalysts decreased in the order PtPd/USY > PtPd/SiO_2-Al_2O_3 > PtPd/γ-Al_2O_3. The sulphur content of feed reduced the hydrodearomatization and hydrocracking activity of the catalysts in different extents. Our results showed that the PtPd/USY catalyst had the highest sulphur resistance.

The HDA activity decreased, the HDS activity increased and the HDN activity increased in the beginning, then peaked at Pd/Pt mass ratio 2:1 (Pd/Pt atomic ratio 3.7:1) finally slowly decreased as the Pd/Pt ratio increased. According to the results of the preliminary experiments, catalyst possessing Pd/Pt mass ratio of 2:1 showed the best performance.

The main goal of our experiments was to find a PtPd/support catalyst which is suitable for deep hydrodearomatization and further deep hydrodesulphurization of gas oils (prehydrogenated in first step of two-stage hydrogenation process) containing up to 300 mg S/kg sulphur and up to 200 mg N/kg nitrogen in second step of two-stage deep gas oil hydrogenation process.

The relatively high hydrodearomatization- and hydrodesulphurization activity and the low hydrocracking activity of PtPd/USY catalyst provides the flexibility of two-step deep hydrodesulphurization and deep hydrodearomatization processes. This means, that by applying this catalyst hydrodearomatization and hydrodesulphurization of different feeds having relatively high sulphur and nitrogen content can be performed with high gas oil yield. Therefore it is not necessary to apply deep hydrodesulphurization to maximum 50 or 10 mg S/kg in the first stage on transition metal/support catalysts.

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