

PERFORMANCE COMPARISON OF CONVENTIONAL AND Y-ZEOLITE-CONTAINING HYDROTREATMENT CATALYST IN HYDROREFINING OF MIDDLE FUEL DISTILLATES DERIVED FROM DIFFERENT SOURCES

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Abstract. In the presented paper we report the performance of a NiMo/(93 % wt. γ -Al₂O₃, 7 % wt. Y-zeolite) catalyst in comparison with the conventional NiMo/ γ -Al₂O₃ catalyst in reactions of hydrodesulphurisation and hydrodenitrogenation that occur during hydroprocessing of middle fuel distillates. The performance evaluation tests were carried out at a flow, high-pressure fixed bed reactor system with real industrial feeds - PGO (primary gas oil from atmospheric distillation) and RHC-GO (gas oil from residual hydrocracking). The results revealed that the NiMo catalyst with an Y-zeolite ingredient has higher desulphurisation activity in the case of PGO treatment and higher denitrogenation activity in the case of RHC-GO than the conventional NiMo/Al₂O₃ catalyst. The addition of Y-zeolite (7 % wt.) into the support of NiMo/Al₂O₃ catalyst enhances its acidity and thereby probably increases its activity for cleavage of C-N and C-S bonds that is necessary for removal of these atoms from the compounds present in the feed.

Key words: hydrodesulphurisation, hydrodenitrogenation, NiMo catalyst, Y zeolite

Introduction

Catalytic hydrorefining is one of the main processes in the petrochemical industry, which plays an important role in refining fractions used as a feed in other processes, e. g. hydrocracking, cracking or reforming. Generally speaking, hydrorefining consists in removing sulphur, nitrogen, oxygen and metal atoms. These reactions are accompanied by hydrogenation and hydrocracking.

Due to an increasing demand for engine fuel, heavy petroleum distillates or liquids from tar sands and shale sources, usually containing larger amounts of heteroatoms, especially nitrogen, are subjected to hydrorefining. Nitrogen compounds, present in these sources, constitute a serious problems, both for producers, as these compounds are responsible for the catalyst poisoning during refining processes, and for consumers, because these compounds are responsible for the degradation observed in fuels during storage and handling.

Catalysts containing Mo or W on γ -alumina carrier with promoters, such as Co or Ni, are commonly used in the hydrotreating process. Over the past decade extensive research studies have been devoted to developing improved catalysts for the process. Most of these studies involve the usage of new or modified support materials [1-5], incorporation of additional promoters [6-10], modification and optimisation of preparation procedures and increase in metal loading [11].

In the presented paper, we report the performance of the NiMo/(93 % wt. γ -Al₂O₃, 7 % wt. Y-zeolite) catalyst in comparison with the conventional NiMo/ γ -Al₂O₃ one. We investigate the influence of the Y-zeolite presence in the conventional hydrorefining catalyst on its hydrodenitrogenation and hydrodesulphurisation activity.

Experimental

Preparation of zeolite component. The starting material for the preparation of zeolite component of the support was NaY (Si/Al = 2.3) synthesized in VURUP, Slovakia. The ammonium form of zeolite was prepared by decationisation using aqueous solution of ammonium nitrate (1.0 M) at 90 °C. By repeated decationisation, 83 % of sodium present in the parent NaY sample was removed. Then the zeolite was thermally treated in „deep bed,, conditions at 580 °C (SY214C). The thermally stabilized sample was again treated with aqueous solution of ammonium nitrate (NH₄SY214) to remove the rest of sodium cations, which were present in the zeolite before stabilization, and also the cationic forms of Al, if they were formed during dealumination. The crystallinity of the sample was checked by X-ray method, the acidity was determined by means of TPD (temperature programmed desorption) of ammonia as described in [12]. The activity was investigated by n-hexane cracking at 350 °C and the molar framework Si/Al ratio was calculated from IR (Infra-Red) data.

Preparation of support. Alumina was prepared from alumina hydrate (Böhmit), which was peptised (5-6 hours) and subsequently it was extruded. The extrudates were dried and calcined in air for 3 h at 500 °C.

The modified support was prepared by mixing peptised alumina (93 wt. %) with the zeolite component (7 wt. %). This mixture was processed in the same way as the pure alumina support, i. e. extruded, dried and calcined in air for 3 h at 500 °C.

Preparation of catalyst. Both Mo/g-Al₂O₃ and NiMo/(γ -Al₂O₃ + 7 wt. % Y) catalysts were prepared by successive wetness impregnation of the extrudates. At first, Mo was deposited on

the extrudates by the „slurry impregnation method,, described in [13] where slurry of a fine powder of MoO_3 and water was used instead of the solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$. The slurry of the extrudates, water and MoO_3 powder, was heated under the reflux at 95 °C. The fine powder of MoO_3 from the slurry disappeared after about 3-5 hours of treatment. Then the extrudates were calcined at 500 °C for 3 hours and afterwards they were impregnated with a solution of Ni acetate. Finally the extrudates were calcined at 500 °C for 3 hours to obtain activated oxide catalysts containing 4 wt. % of NiO and 12 wt. % of MoO_3 .

Before the tests, catalysts were sulphided for 12 hours at 270 °C, 2.7 MPa of hydrogen, and $\text{LHSV} = 2.5 \text{ h}^{-1}$ with PGO in which the content of sulphur was risen by adding CS_2 to 2.5 wt. %. Afterwards the temperature was increased to 360 °C and the sulphidation continued for the next 10 hours. After this period the concentration of H_2S in off-gas remained constant.

Labelling of catalysts. NiMo/g- Al_2O_3 catalyst was labelled as KALex, NiMo/(g- $\text{Al}_2\text{O}_3 + 7 \text{ wt. \% Y}$) as KY214C and the zeolitic component as $\text{NH}_4\text{SY214C}$.

Feedstock properties. As a feedstock in this work were used the primary oil from atmospheric distillation (PGO) and the gas oil from residual hydrocracking (RHC-GO). The characteristics of these fractions were as follows:

PGO:

IBP: 211 °C

3 % - 250 °C, 5 % - 254 °C, 91 % - 350 °C

FBP: 367 °C

Flash point: 80 °C, Cloud point: -2 °C, Pour point: -10 °C

Sulphur content: 0.87 wt. %, Nitrogen content: 263 mg/kg wt.

Colour: clear

RHC-GO:

IBP: 223 °C

5 % - 253 °C, 50 % - 310 °C

FBP: 370 °C

Sulphur content: 0.08 wt. %, Nitrogen content: 1998 mg/kg wt.

Colour: red brown

Apparatus. The catalysts were tested at a flow, high-pressure laboratory reactor with the volume of catalyst bed 10 cm^3 . Thermocouples inserted into the catalyst bed and the reactor coat were used to monitor reaction temperature at various points. Samples from which sulphur and nitrogen were to be determined represent products that were collected for 1 hour at steady state conditions.

Reaction conditions. The hydrotreating of middle fuel distillates was carried out under the following conditions: temperature 340, 360 and 380 °C; hydrogen pressure 2.7 and 3.7 MPa; liquid hourly space velocity (LHSV) 1 and 2.5 h^{-1} ; volume ratio of H_2 /feed 278 and 696 h^{-1} .

Analytical. The amount of sulphur was determined by energy-disperse X-ray fluorescence spectroscopy (Oxford Lab-X 3000).

The nitrogen content in liquid samples was determined by the method of oxidative combustion using chemoluminescence detector (Dohrmann DN 10).

The gases from hydrotreating of middle distillates were analysed by gas chromatography using column PONA (Crosslinked Methyl Silicone Gum) 50 m \times 0.2 mm (Hewlett-Packard 5890 II).

Results and Discussion

The characteristics of the components of the catalyst carriers are given in Table 1.

Table 1. Characteristics of the components of the carriers

Sample	Si/Al (IR)	Si/Al (ch. a.)	Acidity * mmol a.s/g	n-C ₆ conv. ** (starting)	TON mg n-C ₆ /a.s.h
NaY	-	2.3	0.01	0.03	-
$\text{NH}_4\text{SY214C}$	5.28 ± 0.26	2.7	1.16	64.05	1935
Alumina	-	-	0.04	0.01	-

* desorption of ammonia from 220 °C,

** determined from the linear dependence of the $\ln t$ (t = time on stream) vs. \ln conversion for $\ln t = 0$, ch. a. = chemical analysis, a.s. = acid sites

TPD spectra of the ammonia desorption from the components of the catalyst carriers are given in Figure 1. They confirm that alumina compared with $\text{NH}_4\text{SY214C}$ zeolite has a significantly lower number of acid sites and that this fragment of acid sites has a seemingly lower strength compared with the zeolite. Thus it can be concluded that in spite of the relatively small amount of zeolite in alumina the acidity of this modified carrier will partly increase. The X-ray spectra of zeolitic component showed that after a „deep bed,, treatment the crystallinity of $\text{NH}_4\text{SY214C}$ sample was preserved.

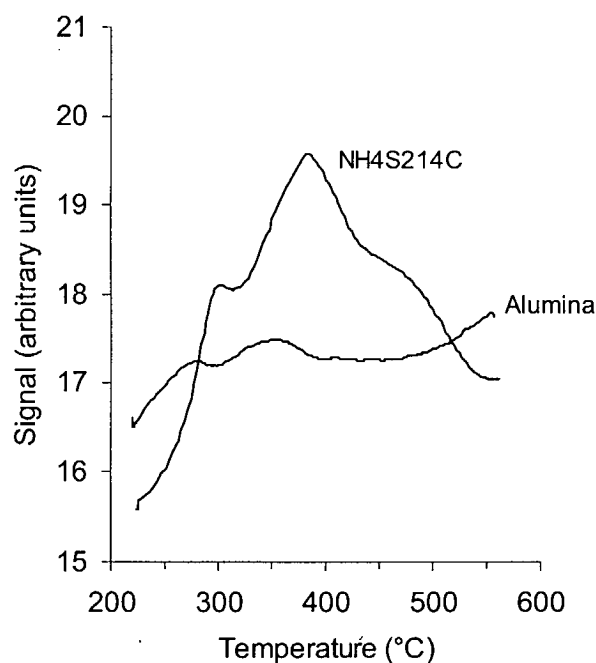


Figure 1. Curves of TPD of ammonia on $\text{NH}_4\text{SY214C}$ and Alumina

As to the products, gaseous stream was analysed by gas chromatography. The analysis showed that in the off-gas predominantly C_3 hydrocarbons were present and that the concentration of hydrocarbons in the off-gas was below 0.5 wt. %. The yield of liquid products under the reaction conditions ranged between 88.5 - 95.6 wt. %. They indicate that the catalysts have acceptable cracking activity.

Hydrodesulphurisation

Process pressure. The effect of process pressure and reaction temperature on the degree of desulphurisation of the feeds is depicted in Figures 2 and Figures 3. Results show that at the given reaction temperatures the increase of the process pressure from 2.7 to 3.7 MPa at WHSV 2.5 h⁻¹ at both investigated catalysts practically does not affect the degree of desulphurisation of PGO (Figure 2) but significantly increases the degree of desulphurisation of RHC-GO (Figure 3).

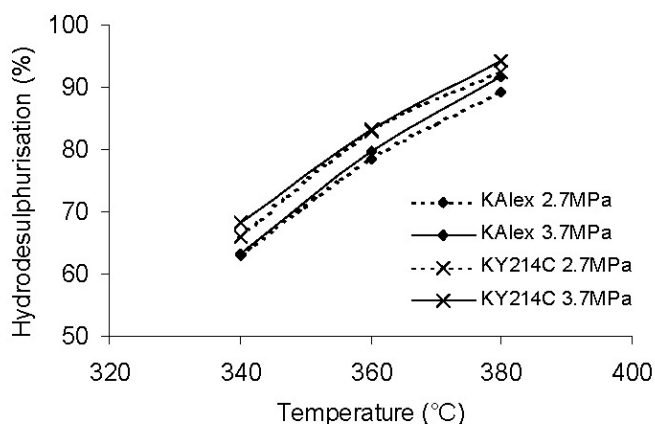


Figure 2. Influence of temperature and process pressure on the degree of desulphurisation of PGO at WHSV 2.5 h⁻¹, H₂: feed = 278 vol.

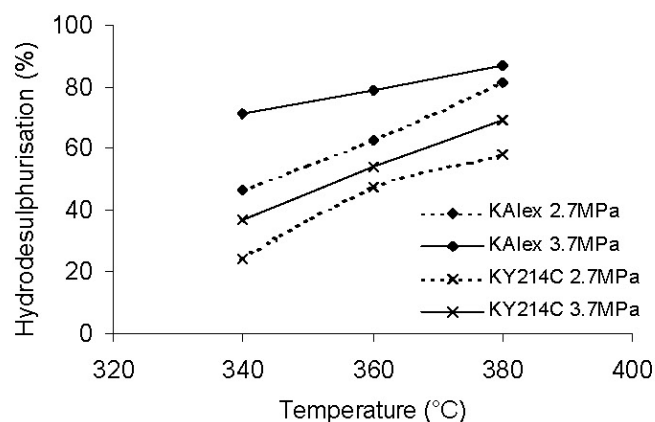


Figure 3. Influence of temperature and process pressure on degree of desulphurisation of RHC-GO at WHSV 2.5 h⁻¹, H₂: feed = 278 vol.

When we compare the desulphurisation activities of catalysts the degree of desulphurisation of PGO at both pressures is a little bit higher with the catalyst KY214C.

The desulphurisation of RHC-GO is not an important question, because the sulphur content in this feed is very low (0.08

wt. %). However, surprisingly enough in the case of this feed at both reaction pressures (Figure 3) the evidently higher desulphurisation activity has been performed by catalyst KAlEx.

LHSV

Figures 4 and Figures 5 demonstrate the influence of LHSV and the reaction temperature on desulphurisation of PGO and RHC-GO. The influence of space velocity was tested at two various LHSV, 1 and 2.5 h⁻¹ at 2.7 MPa and reaction tempera-

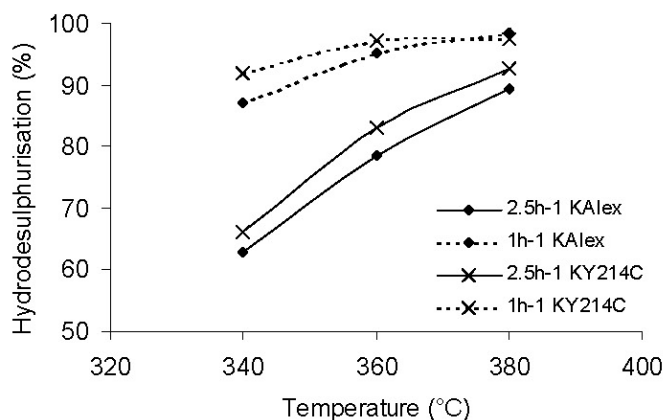


Figure 4. Influence of temperature and LHSV on the degree of desulphurisation of PGO at 2.7 MPa, H₂: feed = 278 vol.

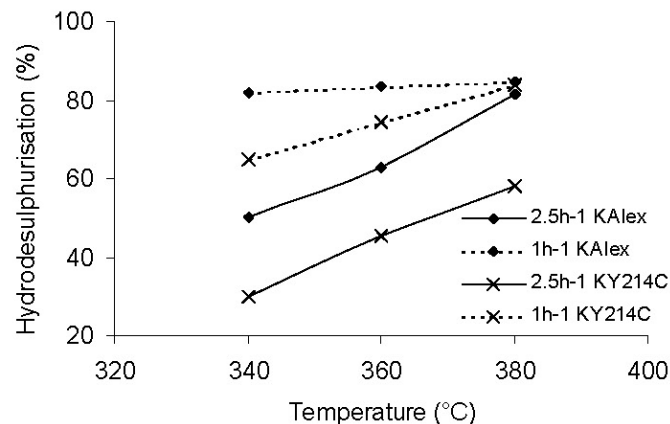


Figure 5. Influence of temperature and LHSV on the degree of desulphurisation of RHC-GO at 2.7 MPa, H₂: feed = 278 vol.

tures 340, 360 and 380 °C.

The results showed that with tested catalysts the decrease of LHSV from 2.5 to 1 h⁻¹ at 2.7 MPa positively affects the degree of desulphurisation of both PGO and RHC-GO feeds.

From Figures 2 and Figures 4 it can be seen that the degree of desulphurisation of PGO with both catalysts is much more affected by the decrease of LHSV from 2.5 h⁻¹ to 1 h⁻¹ than by the increase of the process pressure from 2.7 to 3.7 MPa. In the case of RHC-GO (Figures 3 and 5) both the decrease of contact time as well as the increase of process pressure significantly boost up the degree of desulphurisation of this feed with both catalysts.

Generally it can be summarised that in hydrodesulphurisation of PGO at all investigated reaction conditions, KY214C

with zeolite ingredient has a higher activity than the conventional KAl₂Si₂O₇ catalyst. In conversion of RHC-GO on the contrary to PGO at applied reaction conditions the KAl₂Si₂O₇ catalyst has evidently higher desulphurisation activity than KY214C catalyst.

Hydrodenitrogenation

Process pressure

The denitrogenation activity of tested catalysts in dependence on reaction temperatures at two process pressures 2.7 and 3.7 MPa at LHSV 2.5 h⁻¹ are graphically presented in Figure 6 and Figure 7.

In Figure 6 it can be seen that the degree of denitrogenation of PGO at 2.7 MPa with both catalysts is very similar. When the pressure was increased from 2.7 MPa to 3.7 MPa the denitrogenation activity increased much more with the catalyst KY214C. The result of this fact was an evidently higher denitrogenation activity of KY214C.

On the contrary, the increase of the process pressure from 2.7 to 3.7 MPa practically does not affect the degree of denitrogenation of RHC-GO (Figures 7) by the tested catalysts. As to the activity of the catalysts, the degree of denitrogenation of RHC-GO at both reaction pressures is 5-7 % higher with the KY214C catalyst compared to the KAl₂Si₂O₇ catalyst.

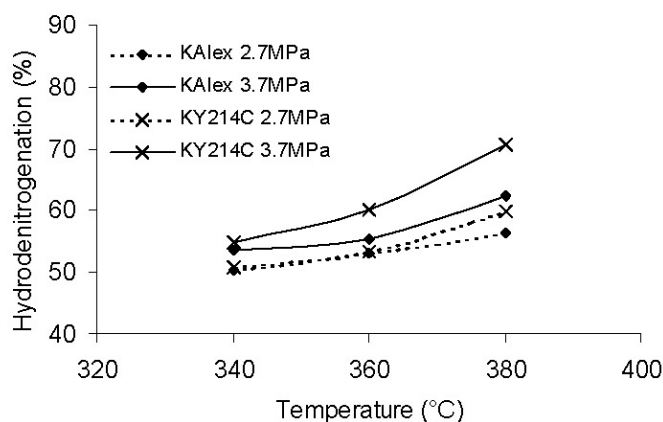


Figure 6. Influence of temperature and process pressure on the degree of denitrogenation of PGO at LHSV 2.5 h⁻¹, H₂: feed = 278 vol.

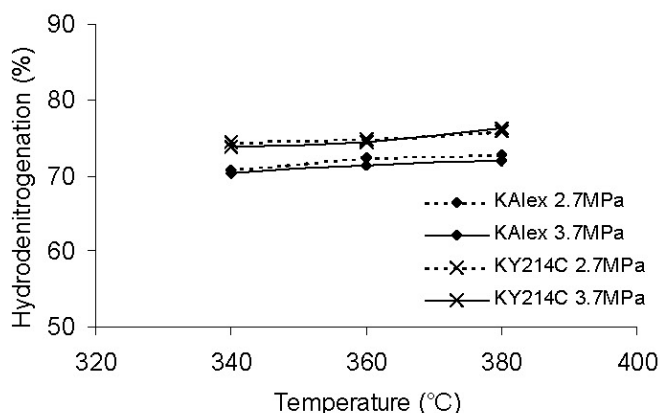


Figure 7. Influence of temperature and process pressure on the degree of denitrogenation of RHC-GO at LHSV 2.5 h⁻¹, H₂: feed = 278 vol.

LHSV

The results of the study of WHSV influence on denitrogenation of PGO and RHC-GO are plotted in Figures 8 and 9.

We can see that at LHSV 2.5 h⁻¹ the activity of both tested catalysts in denitrogenation of PGO is practically the same. By reducing of LHSV at 2.7 MPa from 2.5 to 1 h⁻¹ the degree of denitrogenation of PGO (Figure 8) with both catalysts evidently increases. At LHSV 1 h⁻¹ a clearly higher denitrogenation activity is manifested by the catalyst KY214C.

The degree of denitrogenation of RHC-GO with both catalysts at decreased LHSV from 2.5 h⁻¹ to 1 h⁻¹ at 2.7 MPa (Figure 9) changed much less than it was observed in the case of PGO. However, at both contact times the denitrogenation activity of KY214C catalysts is slightly higher and this activity distinction rises for the benefit of KY214C with decreasing LHSV.

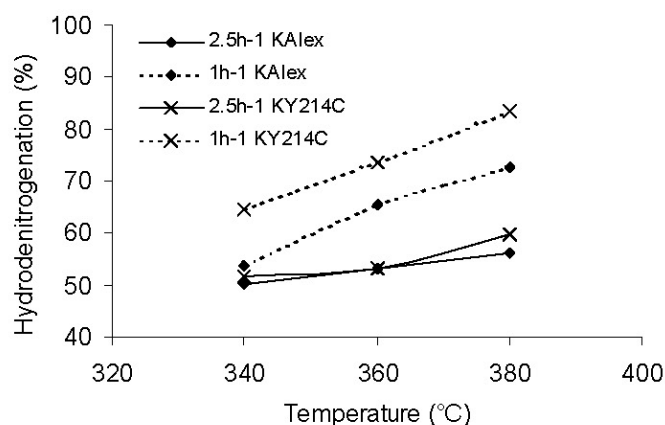


Figure 8. Influence of temperature and LHSV on the degree of denitrogenation of PGO at 2.7 MPa, H₂: feed = 278 vol.

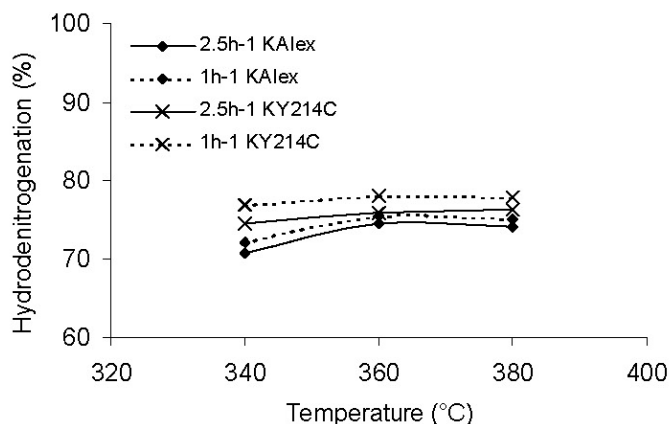


Figure 9. Influence of temperature and LHSV on the degree of denitrogenation of RHC-GO at 2.7 MPa, H₂: feed = 278 vol.

Nevertheless, the degree of denitrogenation of RHC-GO with both catalysts is relatively high (70-78 %) and only slightly depends on the reaction temperature. Under all investigated reaction conditions, although only by 5-7 %, was higher the activity of catalyst KY214C.

From the performance of both catalysts in desulphurisation and denitrogenation of gas oil fractions derived from different sources follows that the type of sulphur and nitrogen com-

pounds in this feed have to be different. In both catalysts the desulphurisation degree of PGO is not affected by increased reaction pressure from 2.7 to 3.7 MPa, but in the case of RHC-GO the pressure increase evidently has a positive effect on the degree of desulphurisation of the feed. The denitrogenation degree of PGO with tested catalysts is positively affected by the increased process pressure from 2.7 to 3.7 MPa, while the denitrogenation degree of RHC-GO with both catalysts at increased pressure does not change.

The surprise is that in all reaction conditions the degree of desulphurisation of RHC-GO is markedly higher with the conventional KAlex catalysts while in the case of PGO it was just vice-versa. To elucidate this fact more detailed study would be necessary. One of the possible explanations could be that it is a consequence of the type and amount of N-compounds present in this feed. Probably N-compounds in RHC-GO are firmly and preferentially adsorbed on active sites present in zeolite-containing catalysts, which has a negative effect on the reaction rate of desulphurisation.

In the case of nitrogen compounds it was reported [14] that acid sites cleave C-N bond and that hydrogenation of unsaturated rings precedes the C-N bond cleavage in the compounds containing nitrogen in a ring position. But it was also reported [15] that hydrodenitrogenation of indoline type compounds can proceed via hydrogenolysis forming ammonia and alkylaromatic compounds. In both mechanisms acid sites play an important role and both hydrogenation and cracking activity are very important in decomposition of nitrogen compounds. From denitrogenation activity of catalysts can be deduced that the higher denitrogenation activity of zeolite containing catalysts can be connected with the acidity of the alumina-zeolite carrier.

Conclusions

The main function of hydrotreatment catalysts in refining of primary gas oil (PGO) is the removal of a sufficient amount of sulphur according to the qualitative requirements for the products because the nitrogen content in this feed is relatively low and, moreover, in the hydrotreated products is not prescribed. At our reaction conditions in dependence on the reaction temperature, pressure and contact time the degree of desulphurisation of PGO over conventional KAlex catalyst varied from 60 up to 90 %, with the catalyst KY214C from 75 up to almost 100 %, respectively. Simultaneously depending on the reaction conditions the degree of nitrogen removal varied with both catalysts between 50-85 %. From this point of view the catalyst based on alumina containing Y zeolite is more effective catalyst for desulphurisation of primary gas oil.

In the case of residual hydrocracking gas oil (RHC-GO) there is no problem to obtain the prescribed content of sulphur by hydrotreatment. But in the hydrotreated product remains relatively high content of nitrogen because of the very high content of it in RHC-GO feed. The observed low colour stability of hydrotreated RHC-GO is dedicated by that time mainly to the nitrogen compounds present in this feed. The degree of denitrogenation of RHC-GO at the given reaction conditions with KAlex was about 71-72 %, with the catalysts KY214C it was in the range 74-78 %. It is probable that the differences will grow with increasing process pressure. The results indicate that the addition of Y zeolite into hydrotreatment catalyst could increase its denitrogenation activity in processing of RHC-GO. The optimisation of zeolite content in the catalysts, the procedure of its preparation and the conditions of catalysts pretreatment could lead to the development of very active catalysts for denitrification of the fuel fractions obtained from residuum hydrocracking processes.

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