HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 38(1). pp. 71-76 (2010)

INVESTIGATION OF ISOMERIZATION OF SULPHUR CONTAINING HEXANE FRACTIONS

ZS. SZOBOSZLAI✉, J. HANCSÓK

Department of MOL Hydrocarbon and Coal Processing, University of Pannonia
8200, Veszprém Egyetem u. 10, HUNGARY,
✉E-mail: szzsolt@almos.uni-pannon.hu

The main activations of gasoline R&D activities simultaneously the stricter environmental requirements and quality specifications based on increased activity catalysts which saving more energy and feedstock. In the EU the gasoline sulphur content was limited to 10 mg/kg and aromatic content was reduced to 35 %v/v in the year of 2005. The benzene concentration was maximized in 1.0%. These specifications with vehicle R&D contributing to the cleaner environment opposing the constantly increase vehicle number/population. At present only cyclo- and isoparaffin concentration are not limited because these components burn cleaner have high octane number, low sensibility, and better combustion properties than the aromatic and olefin hydrocarbons. The scientific articles and papers did not concerned with the long term effect of sulphur species on isomerization activity, the effects with higher sulphur concentration than the real industrial feedstock was investigated and after the deactivation they do not give any further information that the feedstock quality (distillation properties, hydrocarbon composition, heteroatom content) how influenced long term activity of the catalyst, additionally the economy and safety operation of the technology.

One of main objectives of the research work was to select catalysts that applicable for isomerization and desulphurization in one step. Other objectives of our research work were the catalyst selection and process parameters estimation, which could be used in sulphur-containing n-hexane fractions economically feasible, one-step isomerization and desulphurization. In addition, our goal was to determine and estimate those sulphur concentrations, which cause not or only reversible changes in the isomerization activity of the applied catalysts, thereby contributing to faster and safer operational response because of the unexpected change (e.g. increase) in sulphur content of the feedstock.

Our results indicated that relationships were identified between the material composition the catalytic properties and the applied operational combinations (T, P, LHSV, H_2/HC), and available of product qualities. Investigation of the activity of three naphtha isomerization catalysts was studied. We studied the changes in the catalytic activities and selectivities in case of the $Pt/Al_2O_3/Cl$ catalyst, different platinum containing Pt/H-MOR catalysts (metallic/acid sites ratio changes) and the $Pt/SO_4^{2-}/ZrO_2$ catalyst in case of different sulphur containing (<1–120 mg/kg) hexane fractions under the applied process parameters. The range of process parameters were T: 140-280 °C, P: 30 bar, LHSV: 1.0–4.0 h^{-1}, H_2/HC: 1:1-3:1. The main conclusions were that both the $Pt/Al_2O_3/Cl$ and $Pt/SO_4^{2-}/ZrO_2$ catalysts isomerization activity was substantially reduced in case of low sulphur containing feed (5–20 mg/kg), after a short period of time (20–50 hours). The practically sulphur free feedstock (≤0.5 mg/kg) increased the isomerization activity, but it did not regained the starting activity, so deactivation was partly irreversible. H-MOR catalysts with increased (0.4 to 0.6%) Pt-containing was found to be most appropriate, so a slight increase in the concentration of Pt (0.35 and 0.40% to 0.45%) significant (hydrogenation) activity change could be achieved. According to the in case of high sulphur content (~100 mg/kg) feedstock the isomerization activity did not decreased significantly in activity, as well as the sulphur content of the gained liquid products was less than 10 mg/kg for the favorable parameters. This is mainly due to the interaction between Pt and acid sites explained resulting in sulphur-containing compounds weakly bound to Pt surface. We found that the tested catalysts were economically feasible in the one-step isomerization and desulphurization so the increased Pt-containing H-MOR catalysts are the most appropriate, they can significantly increase the flexibility and economy of technology with low cost, as opposed to non-modified catalysts (not integrated into the feed). On the modified, improved Pt-containing H-MOR catalysts the octane number of gained liquid products 30-35 units higher than the feed for the favorable operational parameters (T: 260–270 °C; LHSV: 1.0 to 1.5 h^{-1}, P: 30 bar).

Keywords: Isomerization, desulphurization, one step, light naphtha

Introduction

The most valuable engine gasoline blending components are the iso- and cycloparaffins, because their application causing lower environmental-, human biology risks, that the aromatic or olefin hydrocarbons. However, the availability of iso- and cycloparaffins is limited. Light naphtha yields of different types of crude are different, and these fractions (C_5-C_7) having different amounts of heteroatoms (mainly sulphur compounds), as well as normal- and iso- cycloparaffins, and benzene. The modern motor gasoline and stricter quality requirements become more stringent around the world (reduced sulphur, olefin and benzene concentration). These requirements, together with the vehicle and powertrain developments have being contributing to a cleaner environment. Currently, only the cyclo- and isoparaffins do not limit the amount of engine gasoline because their relatively clean burning, high octane, lower sensibility and better combustion properties, such as aromatic or olefin hydrocarbons. Therefore, demand is growing in number [1, 2, 3]. Under the catalytic conversion of sulphur containing light naphthas the sulphur species was more strongly bonded to the catalytic metal (hydrogenation/dehydrogenating) functional spaces, which causes coke formation on catalysts, so it may lead to rapid deactivation.

Experimental

The main purpose of the experimental work to study the catalytic conversion of desulphurization and the isomerization reaction was to study side by side in laboratory scale equipment with different sulphur containing naphtha fractions rich in n-hexane, continuous operation, and to the steady catalytic activity of desulphurization and isomerization [3, 4, 5, 6, 7, 8, 9, 10, 11]. The reason for this was that about, the catalysts of the real (industrial), 20–150 mg/kg of sulphur-containing material only a few results have been released, and their reliability is questionable. Based on the results of experiments with different compositions of catalysts were determined the advantageous composition of the catalysts and the advantageous parameter combinations, where the favorable properties (practically sulphur free <10 mg/kg, and high-octane number) with appropriate liquid product yield process can be reached.

Experimental eqipment

The experiments were made a 200 cm^3 free volume, vertical, high pressure tubular reactor. It contained all the units, which can be found in a desulphurisation and/or isomerization plant [3]. The experimental system contains a gas-control system and the reactor directly (on-line) contacted to gas chromatograph.

Materials

The volume of the catalyst was 80 cm^3, the free volume was filled with inert material (Raschig ring). AR (96%+) CCl_4, propyl-mercaptan, n-hexane (their mixtures), was used as feedstock. These sulphur content changed between <1–120 mg/kg. Linde 4A molecular sieve was used as moisture trap.

Catalysts and test methods

The catalysts were tested for isomerization: $Pt/Al_2O_3/(7–9\%)$ Cl catalyst (in situ chlorinated with CCl_4), Pt/H-MOR catalysts, which noble metal composition/concentration (increased hydrogenation function) from 0.3 to 0.7% ranged between [3, 4, 5, 6, 7] and non-modified $Pt/SO_4^{2-}/ZrO_2$ catalyst. The main properties of catalysts are showed in *Table 1.* Standard test and calculation methods were used in the study. The platinum and chlorine content of catalysts was determined according to the UOP-274 and UOP 291-76 standard. The surface and the acidity of the catalysts with NH_3 adsorption method and the pore volume and pore size (distribution) with mercury penetration method were determined. The hydrocarbon composition of feedstocks and products with ASTM D5134 (2003) standard was determined. The sulphur content of all materials and products (GREENLAB Ltd./Analytik-Jena - Multi EA 3100-type device) with EN ISO 20846 (2003), water content (GREENLAB Ltd./KEM - MKA-610-type device) with ISO 12937:2001 standard was determined.

Table 1: The main characteristics of applied catalysts

Catalyst	**$Pt/SO_4^{2-}/ZrO_2$**	***Pt /H-MOR**	****Pt/Al_2O_3 /Cl**
PROPERTIES			
Pt-content, %	0.415	0.450	0.380
Pt-dispersion, %	69	86	92–96
Acidity, $mmolNH_3/g$	0.56	0.81	
$Sa_{metalic}$ (metal (Pt) surface on the catalyst), m^2/g metal	25.91	37.84	
S_{metal} (specific metal surface), m^2 metal/g cat.	0.108	0.170	
APS (average particle size f the metal), nm	2.01	5.12	
Specific acidity, $mmolNH_3/m^2$ cat.	0.0043	0.0021	
BET surface, m^2/g	130	395	360–430
Microporus surface, m^2/g	12.2	307.6	
Micropore volume, cm^3/g	0.0045	0.1428	
Mezopore volume, cm^3/g	0.2874	0.2641	
Mezo-/micropore volume ratio	63.9	1.85	
Average pore size, nm(Å)	8.5(85)	2.9(29)	

* A modified catalyst properties

** In-situ chlorinated catalysts, so that the modified catalyst in a number of properties can only be estimated

Due to the large number of results on the most important product properties and the best performance is discussed and presented. To demonstrate the effectiveness of the isomerization of 2,2-dimethylbutane (hereinafter referred to as 2,2-DMB) thermodynamic equilibrium concentration level approach was used (DATEC), because this is the lowest rate from the component, and the equilibrium concentration of the test range varies almost exponentially [3, 10], so the changes are clearly traceable. With IAE the efficiency of isomerization values can be monitored, though it is well to approach the equilibrium concentrations, meanwhile the part of the product (isoparaffins) cracked undesired side reactions reducing the rate of return and hence the economy.

$$DATEC_{2,2-DMB,T} = \frac{C_{2,2DMB}}{C_{2,2-DMB;eq.T}}$$

where $DATEC_{2,2\text{-}DMB,T}$: 2,2-dimethyl-butane degree approach of thermodynamic equilibrium concentration at a temperature T; $C_{2,2\text{-}DMB}$: 2,2-DMB concentration in the hexane fraction (%); $C_{2,2\text{-}DMB;eq.T}$: 2,2-DMB thermodynamic equilibrium concentration (%) at a temperature T.

$$IAE = \frac{Yield_{(i\text{-}C_x + c\text{-}C_x)} \times RON_{(i\text{-}C_x + c\text{-}C_x)}}{100}$$

where *IAE:* the absolute efficiency of isomerization, $Yield(i\text{-}C_x + c\text{-}C_x)$: the yield of iso-and cycloparaffins $RON(i\text{-}C_x + c\text{-}C_x)$: iso-octane number and cycloparaffins (practically 100% separation of the n-paraffins)

Process parameters

The experiments were made on started steady state activity catalysts. Based on preliminary results in the experiments 20–30 bar total pressure, 1.0 to 4.0 h^{-1} liquid hourly space velocity and 1,0:1,0–3.0:1.0 H_2:hydrocarbon molar ratio (industrially relevant conditions) was applied. With the systematic changes in the parameters we tried to find combinations, where feeds with various compositions the desulphurization and the isomerization activity/selectivity good as far as it takes place.

Rersults and discussion

The expediently blended sulphur compounds in higher concentrations to n-hexane have significantly changed isomerization reactions especially the isomerization rate and the effectiveness in case of all three (not modified) base catalysts. Mainly in case of the ZrO_2-based catalyst significant isoparaffin content decrease of the liquid products (primarily decreased concentrations of 2,2-DMB) was obsereved, but positive effect of the increase in sulphur content *(Table 2)* was found. The concentration of isoparaffins in liquid products ranged from 68.9 to 84.6%. This value strongly depended on the applied catalyst and the sulphur content of the feed. In case of the lowest temperature active catalytic system ($Pt/Al_2O_3/Cl$) was the most appropriate to the isomerization of hexane fraction with low sulphur content was confirmed. The modified catalysts with differently increased Pt content were much less sensitive to response the changes of feed sulphur concentration so the decrement the yield of isoparaffins were less therefore the octane number decrement were insignificant (that of the sulphur less feeds). Increasing the yield of the liquid product simultaneously with both the small decrement of isoparaffin yield and octane number was just slightly reduced the octane number mass (liquid yield ^{x} octane number).

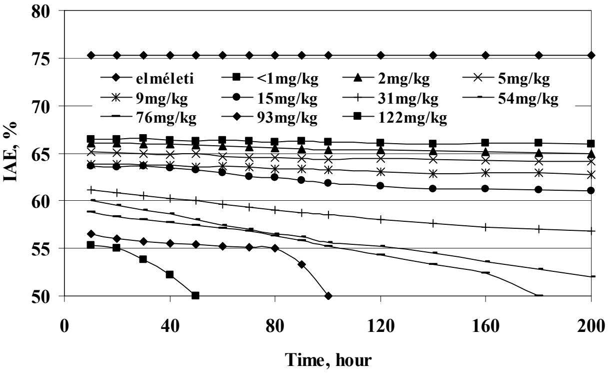

Figure 1: Isomerization absolute efficiency vs. Time in case of different sulphur containing n-hexane feeds on $Pt/Al_2O_3/Cl$ catalyst
(T: 160 °C, P: 30 bar, LHSV: 1,5 h^{-1}, H_2/CH-2:1)

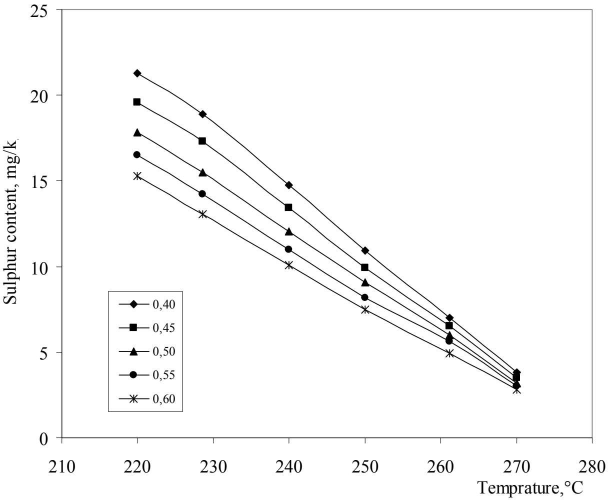

Figure 2: Sulphur content of desulphurised and isomerised n-hexane fraction (85 mgS/kg) vs temperature on different Pt containing H-MOR catalysts
(P: 30 bar, LHSV: 1,5 h^{-1}, H_2/CH-2:1)

In case of high sulphur containing hexane fractions the stricter process parameters were favourable to higher liquid product yields. The concentration of 2,2-DMB in all case were decreased with increasing the sulphur concentration of the feed, while in case of ZrO_2 base catalyst the decrement was much less than the thermodynamic equilibrium concentration. Based on the yield values (Table 2) the best results were gained on $Pt/Al_2O_3/Cl$ catalyst (practically sulphur free feed) in all case, the good choice of chlorine content of the catalyst contributes to the lowest available temperature during isomerization was done, and to reach minimal cracking and more favorable equilibrium product composition. Beyond the change of octane number it is important to note that in case the low sulphur concentration feed (5–10 mg/kg) the selectivity of isomerization reaction was slightly increased nevertheless the conversion rate of isomerization was decreased only a little. These effects and their changes was well correlated the IAE values, which involve both the gained liquid yield and octane number of iso- and cycloparaffin products. With different sulphur containing hexane fractions on 160 °C, 30 bar pressure, 1.5 h^{-1} LHSV, and 2:1 hydrogen/hydrocarbon molar ratio experiments were done, some important results were shown on *Fig. 1* and Table 2.

Table 2: Products from different sulphur containing hexane fractions preferable to find more important features of the operating parameters

Properties			
Catalysts	$Pt/Al_2O_3/Cl$	$Pt/SO_4^{2-}/ZrO_2$	Pt(0.45%)/H-MOR
*Chlorine content of catalyst, %	7.1–9.1	-	-
Sulphur content of the feed, mg/kg	<1–120	<1–50	<1–85
Temperature, °C	150–160	195–200	260–270
LHSV, h^{-1}	1.0–1.5	1.0–1.5	1.0–1.5
Pressure, bar	30	30	30
H_2/CH molar ratio	2:1	2:1	2:1
**Maximum allowable sulphur concentration of the feed, mg/kg	<3	<10	≤~100
Liquid product(C_{5+})			
Yield, %	99.4–98.6	94.5–90.6	96.2–93.7
Sulphur content, %	<1	<1	<10
2,2-dimethylbutane (2,2-DMB), %	27.9–29.8	9.7–11.2	10.8–13.7
$DATEC_{2,2\text{-DMB}}$, %	67.0–78.2	34.0–40.5	48.9–66.4
RON	78.0–74.9	68.2–72.6	71.7–72.8
MON	78.5–75.0	68.3–72.5	71.9–72.5
ΔRON**	44.1–37.6	37.8–33.3	38.0–35.2
Separation of n-paraffins from the liquid product theoretically 100% efficiency			
Yield, %	84.6–77.6	72.5–68.9	75.8–71.9
RON	86.0–86.3	80.0–82.0	82.4–84.6
MON	86.7–86.6	79.7–82.0	82.9–84.4
ΔRON***	53.9–49.9	47.8–46.2	49.0–47.1

* In situ chlorinated catalysts, such as chlorine content and acidity under the measurement can only be estimated, after measuring with the above mention standard test methods

** The highest sulphur content, which is a catalyst capable of reversibly tolerate and the resulting low activity decrement to the technology operate economically

*** The increment of octane number in relation to feedstock

On Fig. 1 the time of isomerization vs. IAE change in case of different sulphur containing hexane feeds shown. It is well illustrated that with less than 5 mg/kg sulphur concentration the isomerisation efficiency just slightly reduced until 100 hour contact time and after that it was nearly constant. Up to 31 mg/kg sulphur concentration of hexane fraction the isomerization activity and efficiency was clearly decreased versus the time. At 54 mg/kg and higher concentration the isomerization efficiency already in the starting period significantly decreased moreover ca. after 150 hour (54 mg/kg), ca. after 90 hour (76 mg/kg), ca. after 60 hour (93 mg/kg), ca. after 40 hour (122 mg/kg) strongly decreased so the catalyst was deactivated. The $Pt/Al_2O_3/Cl$ catalyst only works with very low sulphur containing feeds or it has limited applicability [3, 4, 5, 6, 7]. Differently increased Pt containing (0.3–0.7%) HMOR catalysts activity and selectivity changes were investigated in case of sulphur containing hexane fractions. Hereinafter the 85 mg/kg sulphur containing hexane feed results of one step desulphurization and isomerization is presented. Wit the expediently modified catalysts and the selected process/operational parameters combination (temperature: 220–270 °C, LHSV: 1.0–3.0 h^{-1}, pressure: 30 bar, H_2/hydrocarbon molar ratio 2:1) the result were nearly the same with the results with practically sulphur free feedstock. Simultaneously with the high isomerization activity the catalysts have high desulphurization activity. Because of the acid support electron draw effect the Pt bond strength decreased the sulphur substituent causing the desulphurization to take place rapidly without irreversible poisoning. Based on the datas of Table 2 and *Fig. 2* it was concluded that the desulphurization and isomerization efficiency increased with higher temperature, so the favorable process parameters were temperature: 260 °C, LHSV: 1.5 h^{-1}, pressure: 30 bar, H_2/hydrocarbon molar ratio 2:1. With the applied Pt(0.45%)/HMOR catalyst high octane number, high quality, low sulphur isomerised light naphtha could be produced without long term activity change. In case of the Pt/HMOR catalysts the liquid product octane number were significantly increasing with increased metal/acid site ratio was observed although 0.6, 0.7% Pt content has no significant changes than 0.3 to 0.4–0.5% were raised. We concluded that because of the Pt has high stock price causing relatively high catalyst cost that indicate higher revamp cost and lower return so the higher Pt concentrations are uneconomical.

The other tested catalyst was Pt/sulfated zirconia without any modification so the application was strongly limited or ultra low sulphur naphtha (10 mg/kg) has to be used. Its surface area, specific acidity, pore size and pore volume distributions unbeneficial to forming multibranched isoparaffin mainly the 2,2-DMB were influenced. Increasing the concentration of 2,2-DMB simultaneously increased the gas product yield so the catalyst cracking activity increased which was mainly caused by its physical properties than kinetic effects. In the next section, IAE of the Pt/sulfated zirconia catalyst were presented. *Fig. 3* showed the IAE values in function of time. The explanation of tendency Fig. 3 is that the increasing IAE values of starting period/term of the measurement was the consequence of the decreasing sulphur concentrations (46→0.5 mg/kg), so the catalyst regained (30→48 h) the starting isomerization activity (IAE 62–64% before the measurement, in steady state activity). Repeating the sulphur concentration increasing and decreasing in several periods observed that the IAE values not reached the starting values and isomerization effectiveness consequently the sulphur poising effect was very significant. While the starting period of the IAE reached the 60% (theoretically the highest value: 73%) after in case of sulphur free feedstocks the reduced hydrogenation effect causing relatively high decrement in IAE values. Activity of the metal sites was decreased more and more to a constant value 30%.

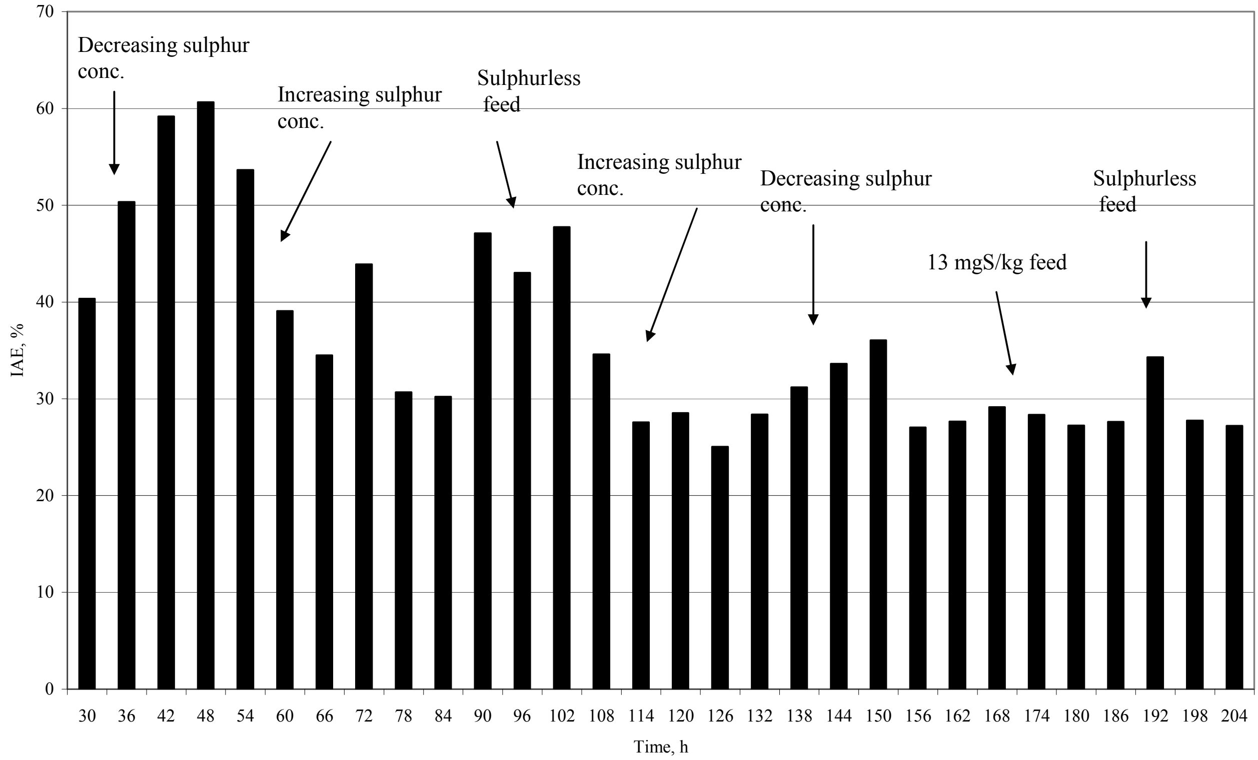

Figure 3: Isomerization absolute efficiency on Pt/sulphated ZrO_2 catalyst (T: 195 °C, P: 30 bar, LHSV: 1,5 h^{-1}, H_2/CH-2:1)

The increase of effectiveness in the period was due to the sulphur free feedstock. In the starting period the in case of sulphur free feedstock slightly activity decrement was observed after the sulphur containing feedstock, further the poising effect in short term was mainly reversible, though these few amount of sulphur was caused a little less isomerization activity decrement but there were increase in the liquid product yield.

The relatively high sulphur concentration (20–46 mg/kg) caused rapid isomerization activity decrease, while the desulphurization efficiency (the amount of removed sulphur / sulphur content of feedstock) was not reduced significantly. In this case, the poisoning effect of sulphur typically occurs irreversibly (short term) of isomerization.

Based on the results, in case of the $Pt/SO_4^{2-}/ZrO_2$ catalyst one-step isomerization and desulphurization the favorable combination of operational parameters and the maximum allowable sulphur content of the feed are: temperature: 195 °C, pressure: 30 bar, space velocity 1.0 h^{-1} feedstock sulphur content: <~10 mg/kg. Through the measurement period in case the 13 mg/kg of sulphur-containing feedstock although not the same extent as the other two sulphur-containing feeds, but also showed some degree of decrease of the isomerization, a longer measurement period the feedstock also may be caused isomerization activity decrement. In fact, the sulphur adsorption took place in case of low concentration of sulphur, so increasing the amount of sulphur in the catalyst.

Conclusions

Only the modified, increased Pt containing H-MOR catalysts of the three investigated isomerization catalysts may be capable of sulphur-containing n-hexane fractions of long term, one-step isomerization and desulphurisation (>20,000 hours) while maintaining profitability. The application pilot plant equipment the investigated catalysts and increased sulphur-containing feeds in industrially relevant conditions made it possible to investigate the conditions and testing examination of the isomerization reactions that affect the effectiveness of the impact study. That kind of catalyst research and results may help the existing processes – flexibility with the changes in feed quality, wide parameter range – for more economical and safer operation. The liquid products yield and octane number can vary considerably, depending on the composition of hydrocarbons (boiling range) and heteroatom containing (sulphur and nitrogen) feedstocks are applied. The investigated catalysts one-step isomerization and desulphurization activity on the favorable technological conditions were as follows: Pt/H-mordenite (increased Pt content) > $Pt/Al_2O_3/Cl$ > Pt/sulfated ZrO_2. The one-step catalytic isomerization and desulphurisation activity was mostly affected by appropriate changing metallic and acid sites ratio. Even deeper known of the physical properties of the catalysts to recognize, and thereby to change the acidity and the specific acidity of the catalysts, metal dispersion and particle size has very significant effect on the catalytic activity showed a primary event. The catalyst had a positive effect by increasing the Pt content of the e^- density of the catalyst active site, and thus the hydrogenation of sulphur compounds takes place more quickly, and the hydrogenation of iso-carbenium ions are less inhibited, so that the products obtained by octane number (composition) is very beneficial to addition to practically sulphur free (<10 mg/kg) as well.

ACKNOWLEDGMENT

We acknowledge the financial support of this work by the Hungarian State and the European Union under the TAMOP-4.2.1/B-09/1/KONV-2010-0003 project.

REFERENCES

1. U. SZALKOWSKA: Fuel quality - global overview, 7th international colloquium on fuels 2009, TAE, Stuttgart/Ostfildern (Germany).
2. H. WEYDA, E. KÖHLER: Modern refining concepts - an update on naphtha-isomerization to modern gasoline manufacture, Catalysis Today, 2003, 81(1), 51–55.
3. J. HANCSÓK, SZ. MAGYAR, ZS. SZOBOSZLAI, D. KALLÓ: Investigation of energy and feedstock saving production of gasoline blending components free of benzene, Fuel Processing Technology, 88 (4), 2008, 393–399.
4. J. HANCSÓK, GY. GÁRDOS, J. PERGER: Isomerisation of Paraffine Hydrocarbons at Low Temperature, Hung. J. Ind. Chem., 15(3), 1987, 309–316.
5. J. HANCSÓK, G. GÁRDOS, M. BAUMANN: The Effect of Platinum Dispersion on the Isomerization of n-Pentane, Hung. J. Ind. Chem., 17(1), 1989, 131–137.
6. J. HANCSÓK, GY. GÁRDOS, B. JUHÁSZ: Development of a Low Temperature Isomerization Catalyst, J. Appl. Chem. (Plenum Publ. Corp.), 62(3), 1989, 569–573.
7. J. HANCSÓK: Izomerizáló katalizátorok savas tulajdonságainak hatása az aktivitásra, Műszaki Kémiai Napok'92, Veszprém, 1992, április 22-24. Kiadvány 108.
8. J. M. SERRA, A. CHICA, A. CORMA: Development of a low temperature light paraffin isomerization catalysts with improved resistance to water and sulphur by combinatorial methods, Applied Catalysis A: General, 239(1-2), 2003, 35–42.
9. G. D. YADAV, J. J. NAIR: Sulfated zirconia and its modified version as promising catalysts for industrial processes, Microporus and Mesoporus Materials, 33, 1999, 1–48.
10. J. HANCSÓK, SZ. MAGYAR K. V. S. NGUYEN, ZS. SZOBOSZLAI, D. KALLÓ, A. HOLLÓ, GY. SZAUER: Simultaneous desulphurization, isomerization and benzene saturation of n-hexane fraction on Pt-H/MOR, Studies in Surface Science and Catalysis - Porous Materials in Environmentally Friendly Processes 158, 2005, 1717–1724.
11. W. TAKEMI, M. HIROMI: Reaction of linear, branched, and cyclic alkanes catalyzed by Brönsted and Lewis acids on H-mordenite, H-beta, and sulfated zirconia. Journal of Molecular Catalysis A. 2005, 239, 32–40.