THESES OF PhD DISSERTATION

INVESTIGATION OF ISOMERIZATION OF LIGHT ALKANES

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1. INTRODUCTION AND OBJECTIVES

Mobility is one of the most important pillars of sustainable development to achieve this modern and environmental friendly (during their life cycle is increasingly less harmful to the environment) motor fuels are required. The gasoline has been long since the most economically and widely produced fuels of spark ignition engines, and they will be expected to remain for the next two or three decades, taking into account the hybrid driving system as well. In case of vehicles equipped with spark ignition engine drive the aromatic and olefin components of gasoline causes mainly the unfavourable compositions of the exhaust gas. The gasoline sulphur content was significantly reduced in several steps (<10 to 15 mg/kg) in the developed regions of the World. Accordingly, beside the increased quantitative requirement of motor fuels their quality requirements were tightened in the last decade (reduction in sulphur, olefin and aromatic components). As a result, gasoline and gasoline blending components of new composition and being derived from renewable sources were appeared showing unconventional physical- and chemical properties.

The conventional blending components have to also be produced with new composition, which contributes to further reduction in the sulphur, aromatic and benzene and the olefin concentrations. Thus the main objective of my research and development work was to produce hydrocarbon mixtures, especially in C₅-C₇ carbon range, of expediently modified composition (isoparaffin rich, reduced benzene and aromatic content, deeply desulphurized:≤10 mgS/kg) with heterogenic catalytic conversion from industrial streams with feedstocks and energy efficient as well as more economical way.

Part of my objective was to developed and investigate the applicability of new catalytic systems those are industrially not common or even not introduced to modify the properties of basic catalysts to determine the combinations of process parameters providing more economical production of the target products.

My important aim also was to produce better blending components in comparing to known ones by applying the obtained research results.
2. EXPERIMENTAL

The experimental system contains two tubular reactor (effective volume: 100-100 cm³), as well as all devices and equipments that are found in the industrial hydrogenation and/or isomerization process loop. The reactors can be operated in serial and parallel furthermore (single)through and recirculation mode.

Model compounds as well as light naphtha fractions of industrial origin (MOL Plc.) were applied as feedstocks. The investigated catalysts were tested in confidential (part of international contract) research and development program or partially prepared/modified them through in this cooperation, and were commercially available (non-modified/base) catalysts.

When it was possible, analytical and performance test methods of the effective gasoline standard were used. In addition, several other physico-chemical and spectroscopic method were used mainly for study of catalysts.

The experiment was carried out long-term series of continuous mode and steady-state activity catalysts (total of 9,000 „operating hours” long).
3. NEW SCIENTIFIC RESULTS

3.1. Isomerization of individual hydrocarbons on Pt/\(\text{SO}_4^2/-\text{ZrO}_2\) catalyst

3.1.1. It was stated that the order of reactivity of the investigated paraffins on the investigated catalyst (under steady state activity) and at applied reaction conditions were the following [5, 17]: n-C_5 < n-C_6 < n-C_7 < c-C_6. It was proved for every investigated hydrocarbon that hydrocarbon partial pressure increase and the hydrogen partial pressure decrease at low pressure and low temperature. The reaction orders were the followings:

- paraffins (\(p_{\text{hydrocarbon}}\): 2-10 bar; \(p_{\text{H}_2}\): 10 bar, constant; \(T\): 150 °C):
  - \(n_\text{n-pentane}\): 0.43; \(n_\text{n-hexane}\): 0.34; \(n_\text{n-heptane}\): 0.39; \(n_\text{cyclohexane}\): 0.24;

- hydrogen (\(p_{\text{H}_2}\): 5-20 bar, \(p_{\text{hydrocarbon}}\): 10 bar, constant; \(T\): 150 °C):
  - \(n_\text{n-pentane}\): -0.79; \(n_\text{n-hexane}\): -0.66; \(n_\text{n-heptane}\): -0.71; \(n_\text{cyclohexane}\): -0.40.

3.1.2. Based on temperature dependence of the initial reaction rates the apparent activation energy values were determined (\(T= 150\text{-}165^\circ\text{C}, p_{\text{H}_2} = 20\ \text{bar}\)). These correspond to the order of reactivity: \(E_{a,n\text{-pentane}}\): 150 kJ/mol; \(E_{a,n\text{-hexane}}\): 122 kJ/mol; \(E_{a,n\text{-heptane}}\): 116 kJ/mol; \(E_{a,\text{cyclohexane}}\): 113 kJ/mol [5, 17].

3.1.3. Considering the formation of individual isomers of the n-hexane and n-heptane it was concluded that first the mono-branched isomers, then the di-branched on different carbon atoms, followed by on the same carbon atoms, and finally the cracked products were formed on the studied catalyst (consecutive reaction path). In case of cyclohexane some products of more than six carbon atoms (such as dimethyl-cyclopentanes, methyl-cyclohexane, etc) were formed, which showed dimerization and/or alkylation and the subsequent cracking.

3.1.4. In case of cyclohexane isomerization at near equilibrium conditions (\(T:190^\circ\text{C}, P:20\text{bar}, \ LHSV:1\text{-}2\text{h}^{-1}\)) the composition of crack products showed that the quantity of isobutane was between 75-90%, which was multiple of the quantity of ethane. It suggests that the cyclohexane ↔ methylcyclopentane (equilibrium reaction) isomerization not only took place in monomolecular reaction on the catalyst, but through formation of \(\text{C}_{12} \rightarrow \text{C}_8\) intermediary molecules, too. The isobutane and the molecules to be mentioned before can also be derived from these intermediates [5, 17].
3.2. Isomerization of binary mixtures on Pt/SO\(_4^{2-}\)/ZrO\(_2\) catalyst

3.2.1. Study of isomerisation of the n-pentane/n-hexane, n-hexane/cyclohexane, n-hexane/n-heptane mixtures was proved that on the same pressure, temperature and liquid space velocity the less volatile (higher boiling) component decreased the rate of isomerization of the more volatile (lower boiling) component in a greater extent than inversely [5, 17].

3.2.2. Study of isomerisation of the n-hexane/cyclohexane mixtures was proved that the value of activation energy obtained at low conversions (P: 20 bar, pH\(_2\): 10 bar, T: 150-165°C) increases with the concentration of the second component. This was true both of the more and less volatile components [5, 17].

3.3. Investigation of isomerization of multiple component mixtures (industrial light naphtha fractions)

3.3.1. Based on the results of experiments to be done with sulphur containing feedstocks (13, 20, 46, 103 mg/kg) it was determined that the isomerization activity of the Pt/SO\(_4^{2-}\)/ZrO\(_2\) catalyst (T:195 °C, P:30 bar, H\(_2\)/hydrocarbon molar ratio: 2.0; LHSV:2.0 h\(^{-1}\)) decreased within a short time (<200 h) in each case. In case of low sulphur containing feedstocks (13, 20 mg/kg) the negative effect was less significant (4-9 abs.%) and it can be compensated by increasing the reactor temperature. In case of low sulphur containing feedstocks (13, 20 mg/kg) the desulphurization activity was high (>90 %) over time. This was partly attributed to the formed also catalytically active ZrO\(_2\)/ZrS\(_2\) system that has not just desulphurization activity but also has isomerization activity after the sulphur poisoning of Pt metal [4].

3.3.2. In case of benzene containing feedstocks it was realised that lower feed preheating temperature can be applied due to the significant amount of heat evolving during the rapid saturation of benzene on the Pt/SO\(_4^{2-}\)/ZrO\(_2\) catalyst, which increases the energy efficiency and decreases the CO\(_2\) emission on the simultaneous/co-processing (benzene saturation and isomerization).

3.3.3. I contributed to developing a new Pt/Al\(_2\)O\(_3\)/chlorine catalytic system (two different chlorine containing alumina catalyst) and technology conditions (using two different processed reactors or properly distributed bed(s) reactor with continuous activator agent input in different concentrations of the feedstocks before the reactors or catalyst beds) for the low temperature (≤120-180°C) „benzene saturating isomerization” process.
Advantages of this process in comparing to the middle temperature benzene saturating processes are feedstock and energy saving, lower CO₂ emission, the octane number of isomerised product is higher in 2-5 units and hydrogen consumption is lower [2].

3.3.4. Based on the results of measurements and calculations obtained on the investigation of the conversion of benzene containing naphtha on the studied catalysts (Pt/\(\text{SO}_4^2-/\text{ZrO}_2\), Pt/\(\text{Al}_2\text{O}_3\)/chlorine, Pt/H-mordenite) it was proved that the benzene has decreasing effect on the octane number (in case of H-mordenite the presence of sulphur) in the investigated temperature range. The reason of this on the one hand the inhibition effect of benzene on the isomerisation (its strong adsorption on platinum and partially covering the acid sites) on the other hand the conversion of benzene to cyclohexane (possibly to methylcyclopentane) of lower octane number. This reducing effect is totally compensated by the difference between octane number of mixture of the formed \(\text{C}_6\) cycloparafins and n-hexane and its isomers. However the octane number of the mixture of cyclohexane and methylcyclopentane is higher than the \(\text{C}_6\) paraffin mixture of isomerised n-hexane in the investigated temperature [1-3, 7-9, 13-15].

3.3.5. Based on the obtained and calculated experimental data of isomerization of benzene containing hexane fractions it was concluded that the saturation of benzene to cyclohexane after its partly isomerization to methylcyclopentane is beneficial. But the ring opening is not because the octane number of mixture of n-hexane and methylpentanes significantly lower than that of the \(\text{C}_6\) cycloparaffin containing mixture is at a specified temperature [1-3, 7-9, 13-15].

3.3.6. Based on the abovementioned it was also realised that the ratio of cyclohexane-methylcyclopentane to be chosen in the feedstock of isomarization so that the total amount of the cyclohexane being in the feed originaaly and formed from benzene should be higher than the thermodynamic equilibrium concentration. This way gives possibility to convert the cyclohexane of 86 research octane number to methylcyclopentane of 91 octane number [6].

3.3.7. It was also recognised that the \(\text{C}_6\) paraffins formed in the ring opening reactions of \(\text{C}_6\) cycloparaffins influences the conversion of the n-hexane in the mixture. This decreases the octane number to be achievable in once through operation of the reactor [6].
3.3.8. It was shown that the Pt/\(\text{SO}_4^2-\)/ZrO\(_2\) catalyst and the enhanced Pt containing (0.45-0.50\%) H-mordenite catalyst further the Pt/Al\(_2\)O\(_3\)/Cl catalytic system suitable for the isomerization of light naphtha fraction containing the light part of the reformate feedstock (primarily benzene, cycloparaffins, i- and n-heptanes) and so increasing octane number of them. By applying the obtained products the benzene content of gasoline can be reduced with 0.5-1.0 absolut percent as well as the total aromatic content with 1-2 absolute percent in comparing to gasolines prepared without this type of isomerate. Of course the reformate pool and its benzene and toluene content will be less because the precursors of these components are not in reformate naphtha feedstock but also in the isomerization feedstock [1-3, 7-9, 13-15].

3.3.9. The high-octane number isomerates contribute to meet the required motor octane number of gasoline (MON) without the research octane number "give away" in refineries. (In the standard specified values usually can only be achieved if the research octane number higher in 1.5 to 2.0 units than the specified.)

3.3.10. Results of isomerization of the cycloparaffin containing mixtures at near equilibrium conversion were consistent with kinetic results and observations being obtained for binary mixtures. This proved that the gained results on the tested Pt/\(\text{SO}_4^2-\)/ZrO\(_2\) catalyst were correct at near industrial conditions, too [6].

3.4. **Investigation of Pt/zirconium-tungsten-oxide catalyst on mesoporous silica support**

3.4.1. It was found that the narrow effective isomerization range of Pt/\(\text{SO}_4^2-\)/ZrO\(_2\) catalyst due primarily to inappropriate size of specific surface area. Based on this the development of a new silica-based catalyst was attended. Experimental data proved that an efficient catalyst of high surface are can be prepared based on silica structured mesoporous SBA-15 catalyst of 700-1000 m\(^2\)/g specific surface area by applying impregnation for introducing the zirconium oxide, tungsten oxide, and optionally silica into the support and the resulting catalysts modified by noble metal, preferably platinum. The prepared Pt-containing catalysts showed higher isomerization activity than that of Pt/\(\text{SO}_4^2-\)/ZrO\(_2\) catalyst did [18].

3.4.2. It was found that the best results can be achieved on the investigated Pt/support catalysts, when the three oxides simultaneously delivered to the surface of the porous SBA-15 support [18].
3.4.3. It was found that favorable process conditions of the isomerization of \( \text{n-pentane} \) on the Pt/\( \text{WO}_x/\text{ZrO}_2/\text{SiO}_2/\text{SBA-15} \) catalyst were the follows: T 205 °C, P: 10 bar, WHSV of 1.5 h\(^{-1}\), \( \text{H}_2/\text{hydrocarbon} \) molar ratio = 5.0, the conversion was 76.07\%, and the i-C5 selectivity were 86.9\% (\( \text{C}_1-\text{C}_4 \): 9.94\% i-pentane: 66.13\%, \( \text{n-pentane} \): 23.93\%) [18].
4. LIST OF ARTICLES AND PRESENTATIONS IN THE TOPIC OF THE PHD DISSERTATION

4.1. Articles and presentation in the field of the dissertation

Revised foreign journal articles


Revised full text presentation in international conference proceedings in English


Revised full text presentation in Hungarian conference proceedings in Hungarian


4.2. PATENT APPLICATION:

5. SUMMARIZED PUBLICATION ACTIVITY

Articles and presentations in the field of the dissertation
- Revised foreign journal articles (English): 6
- Revised Hungarian journal articles: -
- Revised full text presentation in international conference proceedings in English: 5
- Revised full text presentation in Hungarian conference proceedings in Hungarian: 6

Impact factor: 2,194

Revised articles another research fields
Impact factor: 3,407

Total impact factor: 5,601

Total number of publications: 34
Patent application: 1

Total quotation, without self quotation
(in Hungarian and foreign books, in Hungarian and foreign lectorated journals, in foreign patents, in foreign PhD dissertations and studies) 8

Other quotation of the articles
(in Hungarian PhD-, diploma- and other dissertations) 12

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