Conversion of model C₆–C₉ alkanes and straight-run gasoline over Pt(0.1%)-Fe(5%)/Al₂O₃ catalysts promoted with various additives

Arai K. Zhumabekova a, b, Lyazzat K. Tastanova b, c, Raigul O. Orynbassar c, Elvira B. Zhunusova a

a: Chemistry, Chemical Technology and Ecology Department, Kazakh University of Technology and Business, Nur-Sultan 010000, Kazakhstan
b: Chemistry and Chemical Technology Department, K. Zhubanov Aktobe Regional University, Aktobe 030000, Kazakhstan
c: Department of Physical Chemistry, Catalysis and Petrochemistry, Al-Farabi Kazakh National University, Almaty 050040, Kazakhstan

* Corresponding author: lyazzatt@mail.ru

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Abstract
Growing demand for hydrogen promotes the research devoted to the development of new catalysts for hydrocarbons processing in absence of H₂ or at its low concentration. In the present work, it was shown that during the conversion of straight-run gasoline on a zeolite-containing bifunctional catalyst in a hydrogen-free environment cracking, dehydrogenation, isomerization and alkylation take place due to the redistribution of H₂ between initial and formed products directly on the catalyst surface. Fine particles (≤50 Å) localize in zeolite cavities and pores of aluminum oxide, while larger ones are on their outer surface.

Key findings
- High-octane gasoline containing 62.4% isoalkanes and 2.3% aromatic hydrocarbons is obtained on zeolite-containing catalyst at 350 °C with H₂:feedstock ratio = 200:1.
- Decrease in H₂:feedstock ratio to 50 leads to increase of hydrocracking direction, formation of aromatic hydrocarbons and olefins as well as C₁₀–C₁₃ isoalkanes obtained as a result of a disproportionation reaction.
- Decrease in H₂:feedstock ratio leads to essential change in the composition of straight-run gasoline. The presence of aromatic hydrocarbons and olefins, which are octane-forming components, increases the motor properties of gasoline. C₁₀–C₁₃ isoalkanes are the components of diesel fuel.

1. Introduction
Many processes at petrochemical and chemical plants are based on the use of hydrogen or hydrogen-containing gas (HCG) [1–3]. Due to the rapid growth of hydrogen energy application, the shortage and cost of hydrogen are increasing [4–8]; therefore, reducing the consumption of HCG by developing new catalysts and technologies is urgently needed [9–11].

In the literature [12–16] there are data on transformation of model n-alkanes over Pt/zeolite catalysts. During n-octane conversion on Pt/HY catalysts (t = 300 °C, P = 0.18 MPa, H₂/octane ratio is 16 mol.%), selectivity of isomers formation rises from 16.0% (0.02% Pt) up to 80.6% (10% Pt) with increasing platinum concentration. Under these conditions cracking direction decreases from 82.2 to 20.6% [17].

It was shown, that conversion of n-hexane over 0.3% Pt-containing zeolites of L and erionite (E) type is influenced by the degree of ion exchange of K⁺. Under the same conditions (t = 400 °C), the conversion of n-hexane increases from 26.1 to 47.0% with an increase in the degree of ion exchange from 17.0% to 82.0% in L zeolite. According to NH₃ adsorption, three types of acid centers with binding energy (q) equal to 100, 110 and 120 kJ/mol were determined in the catalyst. The highest activity in the n-hexane isomerization reaction is typical for the centers with q = 120 kJ/mol, while the acid centers with lower
binding energy also participate in hydro isomerization but with low efficiency [18]. Molecular sieve effect was shown when comparing the properties of catalysts containing L and E zeolites. On L-zeolite with wide pores (0.71 nm) isomer yield is greater than on E-zeolite with narrowpores (0.36x0.52 nm). In the latter case, the pores are not accessible to branched isomers.

In the present work, conversion of C6–C9 n-alkanes on Pt-Fe/Al2O3+HZSM catalyst modified with additives of cerium, molybdenum and phosphorus in the presence of H2 was studied. Processing of straight-run gasoline was carried out with varying content of hydrogen and in its absence.

2. Experimental

The catalyst was prepared by impregnation of the Al2O3+HZSM mixture with water solutions of Fe(NO3)3-9H2O, (NH4)2MoO4-4H2O, Ce(NO3)3-6H2O, H3PtCl6 and other salts. The wet catalyst sample was formed into granules, dried at 100–250 °C for 5 hours with a heating rate of 20–30 °C/min and calcined at 500 °C for 5 hours.

The catalyst was studied in the reaction of transformation of C6–C9 n-alkanes and straight-run gasoline on the laboratory flow-through unit at the temperatures varying from 280 °C up to 400 °C, the hydrogen pressure of 2MPa, the H2/feed ratio of 200/1, 50/1 and 0/1, and the volume feed rate of 5 h⁻¹. Hydrocarbon composition of the reaction products was analyzed on a "Chrom-4" chromatograph with a stainless steel column filled with γ-alumina oxide by "Supelco". Argon was used as a carrier gas.

3. Results and discussion

The conversion and direction of C6–C9 n-alkanes transformation on the Pt(0.1%)-Fe(5%)/Al2O3+HZSM catalyst modified with various additives is affected by the process temperature under otherwise equal conditions (Pn2 = 2MPa, V = 5 h⁻¹, H2/feedstock ratio = 200/1). Table 1 shows the results obtained at n-nonane processing. As the temperature rises from 300 to 400 °C, the conversion of n-nonane increases from 51.2 to 93.6%.

As shown in Table 1, the olefins formed during dehydrogenation of intermediate activated surface complexes are rapidly isomerized through the carbonium ion formation and hydrogenated to isosalkanes. Due to this, only traces of olefins are present in the products mixture. Other directions of olefins transformation probably include formation of aromatic hydrocarbons (0.1–2.7%) at temperatures of 350–400 °C. The maximum yield of C10–C14 isosalkanes (35.7%) is determined at 350 °C. The assumed mechanism of alkane conversion is possible on the active catalyst sites containing both metal and acid centers.

Figure 1 presents the data on C6–C9 n-alkanes conversion on the Pt-Fe/Al2O3+HZSM catalyst promoted by different additives and the yield of isomers at different temperatures.

With the increase in temperature, conversion of n-alkanes grows, and at 400 °C it reaches 96.7–97.9%. The temperature dependence of maximum yield of isomers is observed at close conversion degrees of C6–C9 n-alkanes. The curves pass through the extrema at 350–380 °C. The maximum yield (1%) decreases in the following series: hexane (32.0%) > heptane (30.6%) > octane (30.3%). In the high temperature area (>350 °C) the formation of aromatic hydrocarbons (0.1–2.8%) and olefins (traces) is observed.

Physical and chemical properties of the polyfunctional, promoted with additives, Pt (0.1%)-Fe(5%)/Al2O3+HZSM catalyst were studied by BET, XRD and electron microscopy (EM) methods. The specific surface area and total pore volume of the catalyst are 179.2 m²/g and 0.40 cm³/g, respectively. The XRD results show that the catalyst is dispersed. HZSM structural elements (reflexes 12.5; 10.9; 9.8; 3.83; 3.70; 3.64; 2.96 Å), Ce (reflex 2.76 Å) (ASTM 38-763), Pt (superimposed with γ-Al2O3, reflex 2.27 Å) (ASTM 4-802), Fe–FeO3 (1.46 Å) (ASTM 16-895), γ-Al2O3 (reflexes 2.40; 1.98; 1.40) are present.

Table 1 Influence of temperature on n-nonane conversion on zeolite-containing Pt-Fe/Al2O3 catalyst (P = 2 MPa, V = 5 h⁻¹, H2/feedstock ratio = 200).

| Products composition, % | Temperature, °C |
|-------------------------|----------------|
|                         | 300 | 320 | 350 | 380 | 400 |
| C6-C8 hydrocarbons      | 1.8 | 10.9| 20.7| 34.3| 36.5|
| C7-C9 isosalkanes       | 20.2| 30.9| 35.7| 33.2| 31.5|
| C8-C9 n-alkanes         | 29.2| 29.4| 26.1| 23.8| 22.9|
| olefins                 | traces| traces| traces| traces| |
| aromatic hydrocarbons   | -    | traces| 0.1 | 0.2 | 2.7 |
| Feedstock               | 48.8| 28.8| 17.4| 8.5 | 6.4 |
| n-nonane conversion, %  | 51.2| 71.2| 82.6| 91.5| 93.6|

Figure 1 Influence of temperature on C6–C9 n-alkanes conversion and yield of isomers (P = 2 MPa, V = 5 h⁻¹, H2;feed = 200/1). 1, 4 – Isoalkanes yield and conversion of n-hexane. 2, 5 – Isoalkanes yield and conversion of n-heptane. 3, 6 – Isoalkanes yield and conversion of n-octane.
The EM study (120000 magnification) showed the presence of an aggregate in the Pt-Fe/Al₂O₃ catalyst modified with cerium, molybdenum and phosphorus, which consists of dense particles of ~200 Å size. The microdiffraction pattern is represented by two rings and can be attributed to FeO₃·Hematite (JCPDS, 35-664). At low magnification, large elastic lamellar crystals with basal reflections on their bends were detected. The microdiffraction pattern can be attributed to FeOOH (JCPDS, 26-792). Small loose clusters of dispersed particles with sizes of 20 Å were found in the sample; according to the microdiffraction pattern, they represent CeO₂ (JCPDS, 34-394). Small loose clusters of ~100 Å particles give a diffraction pattern which can be attributed to a mixture of Pt₃O₄, MoO₃ and CeAlO₃ (JCPDS, 21-1284) and CeAlO₃ (JCPDS, 28-260). Characteristic extensive clusters of 30–40 Å particles of Ce₂O₃ were detected. An aggregate of loose small particles 30–50 Å in size was found, which is a mixture of Ce₂(MoO₄)₂, Ce₂MoO₇ and PtO₂ (JCPDS, 57-330). The sample also contains individual large loose crystals of dense particles with cut features represented by the reflections with hexagonal arrangement, and they are related to FeMoO₄, CeF₂, β-MoO₃ (JCPDS, 37-1445), and PtO₂ (JCPDS, 23-1306).

Nanosized (20–100 Å) homo- and heteroatomic clusters were found in the zeolite-containing Pt(0.1%)-Fe(5%)/Al₂O₃ catalyst modified with phosphorus, molybdenum, and cerium additives. In the calcined catalyst (\(t = 500 ^\circ C\)), platinum (\(d = 30–100 \) Å) and iron (\(d = 200 \) Å) are in the form of oxides. Iron and cerium (\(d = 20–50 \) Å) interact with molybdenum, forming precursors (FeMoO₄, CeMoO₄, Ce₂MoO₇), which transform into heteroatomic Fe–Mo and Ce–Mo nanoclusters in reducing medium.

Analysis of the obtained data on dimensionality and structure of metal particles of the catalyst active phase allows us to conclude that it is possible to synthesize nanocatalysts with given composition and properties by directed selection of precursors.

Presence of phosphorus in the catalyst prevents the formation of heteroatomic Pt–Fe, Pt–Mo clusters, whereas the introduction of molybdenum into the catalyst composition in the absence of phosphorus increases the dispersion of metal particles and promotes the formation of heteroatomic highly dispersed clusters at calcination. However, it cannot be excluded that such heteroatomic clusters may be formed during the hydrogen treatment of the catalyst (350–400 °C). Metal nanoparticles are localized in the cavity and mouths of zeolite and pores of aluminum oxide. In addition, larger 100–200 Å crystals were detected by electron microscopy method on the smooth surface of zeolite. It is known from the literature [19, 20] that reduction of iron (III) into iron (II) and iron (0) is observed under hydrogen treatment of air calcined Pt–Fe/Al₂O₃ – systems [19]. The formation of Pt–Fe clusters, which facilitates and accelerates the reduction of iron, was detected by NGRS method [20].

Zeolite-containing Pt(0.1%)-Fe(5%)/Al₂O₃-catalyst a modified with additives (Mo, Ce, P) were studied in the process of straight-run gasoline hydro refining at varying temperatures (280–400 °C), and H₂:feed ratio (pressure - 2 MPa, \(V = 5 \) h⁻¹).

At temperature rise from 280 up to 400 °C (\(P_{H₂} = 2 \) MPa, \(V = 5 \) h⁻¹, \(H₂:feed=200:1\)), it was shown, that hydrocracking, hydro isomerization and dehydrocyclization are occur on the catalyst at hydro refining of straight-run gasoline. The formation of light C₁–C₇ hydrocarbons occurs at \(t \geq 350 \) °C, and at 400 °C their yield is 17.6% (Table 2). The optimum yield of C₄–C₇ isomers, 62.4%, was determined at 350 °C. At lower and at higher temperatures the yield of C₄–C₅ isomers decreases to 50.5 and 51.3%, C₁₀–C₁₃ isomers - 15.6%, C₄–C₅ n-alkanes - 15.3%, C₁₀–C₁₅ n-alkanes - 0.5% and aromatic hydrocarbons - 2.3% are also present in the product mixture. Olefins appear (0.3–0.4%) at temperatures \(\geq 380 \) °C.

At straight-run gasoline hydro refining, attention was paid to the influence of \(H₂:crude\) ratio on the direction of the process. The data on straight-run gasoline conversion on the Pt-Fe/Al₂O₃ zeolite-containing catalyst at \(H₂:feed=50:1\) are presented in Table 3. In this case, the process was carried out in the temperature range of 350–400 °C. The maximum hydro refining of straight-run gasoline occurs in these conditions. It follows from Table 3, that with \(H₂:feed\) ratio decreasing to 50/1 the isomerizing activity of the catalyst decreases from 62.4 to 54.3%.

### Table 2 Conversion of straight-run gasoline on zeolite-containing Pt-Fe/Al₂O₃ catalyst (\(P = 2 \) MPa, \(V = 5 \) h⁻¹, \(H₂:feed=200:1\)).

| Products composition, % | Process temperature, °C |
|-------------------------|------------------------|
|                         | 280                    | 300                    | 320                    | 350                    | 380                    |
| C₁–C₇ hydrocarbons       | -                      | traces                 | 3.9                    | 10.9                   |
| C₄–C₇ isoalkanes         | 50.5                   | 54.7                   | 56.7                   | 62.4                   | 54.2                   |
| C₅–C₇ isoalkanes         | 20.4                   | 19.5                   | 19.7                   | 15.6                   | 13.8                   |
| C₄–C₅ n-alkanes          | 26.9                   | 23.3                   | 21.1                   | 15.3                   | 18.7                   |
| C₁₀–C₁₅ n-alkanes        | 0.3                    | 0.6                    | 0.7                    | 0.5                    | traces                 |
| aromatic hydrocarbons    | 1.9                    | 1.9                    | 2.0                    | 2.3                    | 2.1                    |
| olefins                  | -                      | traces                 | traces                 | 0.3                    |                       |
| Liquid phase yield       | 100                    | 100                    | 96.1                   | 89.1                   |

### Table 3 Conversion of straight-run gasoline on zeolite-containing Pt-Fe/Al₂O₃ catalyst (\(P = 2 \) MPa, \(V = 5 \) h⁻¹, \(H₂:feed=200:1\)).

| Products composition, % | Process temperature, °C |
|-------------------------|------------------------|
|                         | 350                    | 380                    | 400                    |
| C₁–C₇ hydrocarbons       | 6.3                    | 12.4                   | 21.8                   |
| C₄–C₇ isoalkanes         | 54.3                   | 49.9                   | 42.5                   |
| C₅–C₇ isoalkanes         | 23.5                   | 20.5                   | 16.9                   |
| C₄–C₅ n-alkanes          | 8.1                    | 9.9                    | 11.6                   |
| aromatic hydrocarbons    | 7.5                    | 6.9                    | 6.7                    |
| olefins                  | 0.3                    | 0.4                    | 0.5                    |
| Liquid phase yield       | 93.7                   | 87.6                   | 78.2                   |
Hydrocracking with formation of C₁₆-C₃ hydrocarbons increases from 3.9 to 6.3% at 350 °C. However, at a reduced H₂:feed ratio the yield of C₁₀-C₁₃ isoalkanes rises from 15.6 to 23.5% (350 °C). In all studied temperature range the yield of C₁₀-C₁₃ isoalkanes is higher than at H₂:feed ratio = 200:1. The detected effect of a significant increase in the yield of aromatic hydrocarbons from 2.3 to 7.5% (Tables 2 and 3) is of particular interest. 0.3–0.5% of olefins were found in the products.

In order to elucidate more fully the role of HBG, the study of the catalyst activity in processing of straight-run gasoline in the absence of hydrogen was carried out. It was shown that the yield of C₄-C₉ isoalkanes at 350 °C is 62.6%, and with the rise of temperature up to 400 °C the content of isoalkanes in the product mixture falls to 39.0%. At the same time, there is a disproportionation reaction, which leads to C₁₀-C₁₄ isoalkanes and C₁₀-C₁₃ n-alkanes appearance. Their yields are maximal at 350 °C (14.3% and 4.0% respectively). The most important is the formation of high-octane aromatic hydrocarbons – 5.4% (350 °C) and olefins (6.7%).

4. Conclusions

Thus, in the absence of hydrogen the yield of C₁₆-C₃ isoalkanes is 62.6%, and heavier isoalkanes, aromatic hydrocarbons and olefins appear. Hydrocracking to C₁₀-C₁₃ hydrocarbons increases at high temperatures (380–400 °C). At 350 °C the yield of the liquid phase, i.e. gasoline with a sufficiently high octane number is close to 100%.

The analysis of the particle size of metals included in the catalyst shows that their dispersion varies within a wide range, from 20 to 200 Å. Fine particles (≤50 Å) can localize in zeolite cavities and pores of aluminium oxide, and large ones-on their outer surface. When the catalyst contacts with n-alkanes, the whole surface participates in the process, but formation of branched isomers of C₃+ alkanes is possible only on the outer surface, whereas C₁₆-C₄ hydrocarbons of different structure probably appear in zeolite cavities during cracking transformation of n-alkanes capable of diffusing deep into the matrix structure. Diffusion of molecules and their transformation increase with temperature, which is confirmed by the increase in cracking of n-alkanes.

Supplementary materials

No supplementary materials are available.

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Conflict of interest

The authors declare no conflict of interest.

Author contributions

Conceptualization: A.K.Z., L.K.T.
Data curation: A.K.Z.
Formal Analysis: L.K.T., Y.A.A.
Investigation: A.K.Z., L.K.T.
Methodology: R.O.O., Y.A.A.
Resources: R.O.O.
Supervision: Y.A.A.
Validation: A.K.Z., L.K.T.
Visualization: E.B.Z.
Writing – original draft: A.K.Z., E.B.Z.
Writing – review & editing: L.K.T.

Additional information

Author IDs:
- Lyazzat K. Tastanova, Scopus ID 57202578243
- Raigul O. Orynbassar, Scopus ID 57223975563
- Yermek A. Aubakirov, Scopus ID 55447002200

Websites:
- Kazakh University of Technology and Business, https://kaztbu.edu.kz/
- K. Zhubanov Aktobe Regional University, http://zhubanov.edu.kz/en/
- Al-Farabi Kazakh National University, https://www.kaznu.kz/en

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