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Study of Joint Conversion of Butane and Hexane, Propane and Heptane over a Pt/Al₂O₃ Catalyst

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Abstract

A 0.25 % Pt/ γ -Al₂O₃ catalyst was investigated. The sample was tested in modelling of joint conversion of butane and hexane, propane, and heptane with assessing kinetic parameters of the reactions under study. It was found that a decrease in the activation energy by 10.6 kJ/mol and an increase in the rate constant of aromatization by 1.3 times in comparison with hexane conversion was observed at joint conversion of butane and hexane, which leads to an increase in the yield of aromatic hydrocarbons. At the introduction of propane into the reaction medium to heptane, a reverse dependence was detected.

Key words: propane, butane, hexane, heptane, activation energy, rate constant, aromatic hydrocarbons

INTRODUCTION

Bifunctional catalytic system based on platinum over aluminium oxide is fairly well studied for such important industrial processes as catalytic reforming of benzenes, isomerization of aromatic hydrocarbons, dehydrogenation of *n*-paraffins *etc.* [1–6]. Finding the possibility of using aluminoplatinum catalysts in the reaction of joint conversion of hydrocarbon gases and gasoline fractions [7] has opened up a new area to study these systems, as well as regularities of the reaction behaviour on them.

The prospects of such studies are driven by the fact that technology of joint converting hydrocarbon gases and gasoline fractions allow significantly increasing the yield of high-duty fuel component (with RON of 98 and more) in comparison with the traditional technology of catalytic reforming [8]. Additionally, an increase in the yield of a high-octane gasoline component is ensured due to the inclusion into processing of low-value hydrocarbon gases, most of which currently do not find qualified use.

Earlier [9, 10], we found that catalysts containing electron deficient platinum (Pt^σ centres) on aluminum oxide comprising acid Lewis sites (L₂) with adsorption bands in IR spectra of adsorbed CO 2211, 2230–2235 cm⁻¹. Additionally, in work [11], the impact of effects of carrier modification by hardly reducible metals in the groups III and IV of the periodic table on acidity and catalytic properties of the samples obtained was demonstrated.

The present work demonstrates differences in the catalytic and kinetic reaction parameters of joint conversion of model mixtures: butane–hexane and propane–heptane.

EXPERIMENTAL

Preparation of catalysts

For carrier preparation, powders of aluminium hydroxide with the structure of pseudo-boehmite obtained by the hydrolysis method of aluminium alcoholates were used. The catalyst

carrier was prepared by plastification of AlOOH with an aqueous solution of oxalic acid (acid module : acid/Al₂O₃ = 0.03 (mol/mol)) with mixing followed by moulding in extrudates of 1.5 mm diameter, drying at 393 K and calcining at 793 K. On the calcined carrier, 0.25 mass % platinum from dihydrogen hexachloroplatinat (IV) acid in a mixture with a solution of 0.1 M HCl was applied. Samples dried at 393 K were calcined in a current of dry air at 793 K and then reduced in hydrogen at 773 K.

Catalytic studies

Studies of catalytic properties of samples were carried out on a flow microcatalytic setup with an isothermal plug flow reactor. The set-up was equipped with on-line analysis with sampling from the reaction area. Chromatographic analysis was performed using a Tsvet-800 chromatograph equipped with a J&W Scientific PONA/PIONA column (the USA).

Kh. ch. (chemically pure) reagent grade dry *n*-hexane (*n*-heptane) and liquefied *n*-butane (propane) (concentration of 99.9 %) were used as raw materials. A catalyst fraction with a particle size of 0.2–0.4 mm was used for testing. Into the isothermal area of the reactor, 1 g of the catalyst was loaded by portions diluted with quartz. Catalytic trials were carried out at the temperatures of 460–793 K, pressure of 0.35 MPa and feed space velocities of 3.2–12.8 h⁻¹. The hydrogen consumption was set from a hydrogen/hydrocarbon ratio of 2.5–3.0 (mol/mol). After sampling hexane (heptane) conversion products a mixture of hexane + butane (heptane + propane) in a ratio of 70 : 30 mass % was supplied under the same conditions of the process and equal partial pressures of hexane (heptane) and hydrogen in the both cases. The equality of the partial pressures was ensured by helium supply into the reaction area in amounts equal to those of propane and butane supplied. The raw materials and reaction products were analyzed using on-line chromatographic analysis ensuring the measurement error of no more than 0.5 %.

Calculating hexane (heptane) conversion was conducted according to the formula:

$$X_h = (Y_1 - Y_2)/Y_1 \cdot 100 \%$$

where Y_1 and Y_2 are amounts of submitted and unreacted hexane (heptane), respectively, g.

Calculating butane (propane) conversion:

$$X_b(X_p) = (Y_1 - (Y_2 - Y_3))/Y_1 \cdot 100 \%$$

where Y_1 and Y_2 are amounts of submitted and unreacted butane (propane) and butane (propane) formed from hexane (heptane), respectively, g; Y_3 is amount of butane (propane), formed from hexane (heptane), g. Calculating kinetic reaction parameters was carried out to fit the model of assessing the activity of reforming catalysts in the integral reactor at the temperatures of 733–793 K [12].

RESULTS AND DISCUSSION

To determine the temperature, at which conversion of butane, propane, and a mixture of butane – hexane, propane – heptane is possible, thermodynamic calculations were made. Figure 1 presents the dependence of the Gibbs energy change (ΔG) on the temperature (T , K) for the reactions given. It can be seen that at joint conversion of butane–hexane and propane–heptane, the probability of the formation of xylenes and ethane is fairly high. The formation of the reaction products is possible at a temperature of not higher than 550 K. Herewith, an increase in the reaction temperature leads to an increase in the probability of the formation of aromatic hydrocarbons in the

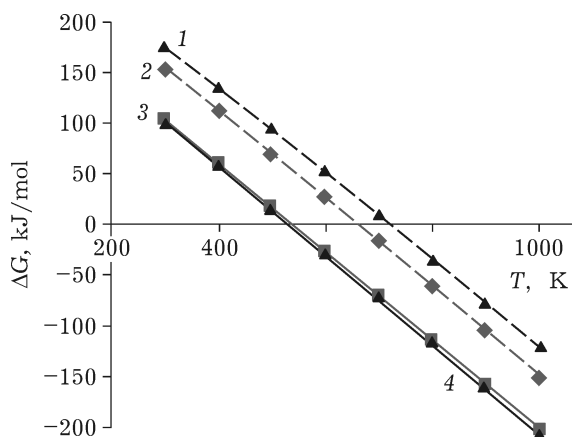


Fig. 1. Thermodynamic probability of hydrocarbons conversion in a temperature range of 300–1000 K: 1 - $C_3H_8 + C_3H_8 = C_6H_6 + 5H_2$, 2 - $C_4H_{10} + C_4H_{10} = C_8H_{10} + 5H_2$; 3 - $C_4H_{10} + C_6H_{14} = C_8H_{10} + C_2H_6 + 4H_2$; 4 - $C_3H_8 + C_7H_{16} = C_8H_{10} + C_2H_6 + 4H_2$.

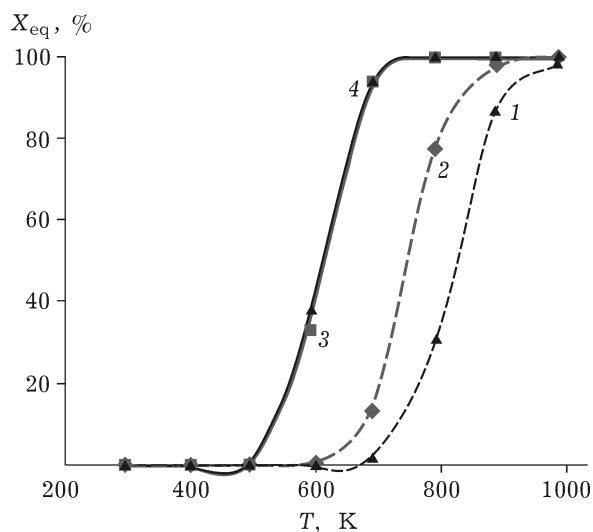


Fig. 2. Equilibrium conversion of butane, propane, as well as their mixture with hexane, and heptane vs temperature: 1 - $C_3H_8 + C_3H_8 = C_6H_6 + 5H_2$; 2 - $C_4H_{10} + C_4H_{10} = C_8H_{10} + 5H_2$; 3 - $C_4H_{10} + C_6H_{14} = C_8H_{10} + C_2H_6 + 4H_2$; 4 - $C_3H_8 + C_7H_{16} = C_8H_{10} + C_2H_6 + 4H_2$.

both cases. The possibility of the formation of aromatic hydrocarbons at the interaction of two butane or propane molecules shifts to the region of higher temperatures by 100–150 K. Additionally, it is noteworthy that the formation of alkanes with a larger molecular mass than for raw material components is impossible in a range of calculated temperatures [9].

The numerical values of the equilibrium conversion of hydrocarbons for the directions described above (see Fig. 1) of joint conversion

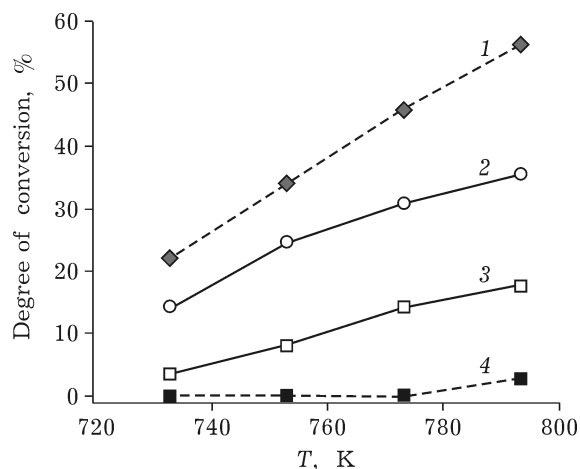


Fig. 3. Conversion degree of propane and butane vs temperature (feed space velocity (FSV) = 3.2 h^{-1}): 1 - butane, 2 - butane + hexane, 3 - propane + heptane, 4 - propane.

are presented in Fig. 2. It can be seen that at the interaction of butane and hexane molecules, as well as propane and heptane with the formation of xylenes and ethane, significant values of the equilibrium conversion are reached at a temperature of 650 K. In case of aromatization of butane and propane, acceptable values of the equilibrium conversion are reached at higher temperatures (near 800 K) due to a lower thermodynamic probability of the performance of these reactions.

Comparative catalytic tests on conversion of propane and a mixture of propane and a mixture of heptane–butane and butane–hexane were conducted. Dependencies propane and butane conversion, as well as at their joint conversion with heptane and hexane presented in Fig. 3. It follows from the data obtained that at the temperatures of 733–773 K, there is no propane conversion. A further increase in the reaction temperature up to 793 K leads to the appearance of propane conversion (2.9%). At the introduction of heptane into the reaction mixture, propane conversion already at a temperature of 733 K is 3.5%, and with increasing the reaction temperature up to 793 K, an increase in the conversion degree up to 17.7% is observed. Unlike propane, the butane conversion degree is 22.0%, and with an increase in temperature, an increase in its conversion to 56.2% occurs at 793 K. In case of joint conversion of butane and hexane butane transformation increases from 14.0% (733 K) to 35.4% (793 K).

Thus, one can note that an increase of propane conversion in comparison with individual conversion is observed at the introduction of heptane into the reaction medium. However, butane conversion in case of joint butane and hexane conversion is higher at individual conversion than at conversion of a binary mixture. Such a regularity of a change in conversion of hydrocarbon gases indicates a complicated mechanism of the molecular interaction.

The major direction of propane conversion is cracking with the formation of methane and ethane, and in butane conversion products, isobutane is present, alongside with the cracking products (methane, ethane, propane). There are no aromatic hydrocarbons in a temperature range of 733–793 K.

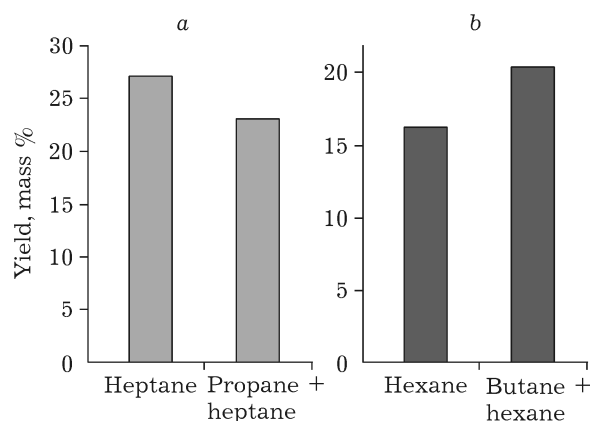


Fig. 4. Yield of aromatic hydrocarbons during conversion of heptane and propane and heptane (a), hexane and butane and hexane (b) ($T = 773$ K, $FSV = 3.2$ h $^{-1}$).

Comparison of the yield of the resulting reaction products at heptane conversion and its joint conversion with propane at a temperature of 773 K demonstrates that the yield of isoheptanes does not change significantly at both individual conversion (85.3 %) and at joint conversion with propane (83.4 %) and amounts to 34.7–35.6 mass %. An increase in the yield of hydrocarbon gases (methane, ethane) at joint conversion of propane and heptane by 4.7 mass % in comparison with heptane conversion is observed. Butanes, pentanes and hexanes, the yield of which is not significantly different depending on the raw type, are also detected in the reaction products.

The yield of aromatic hydrocarbons at conversion of heptane and its mixture with propane is presented in Fig. 4, a. It can be seen that the yield of aromatic hydrocarbons at heptane conversion is 27.1 mass %. The introduction of propane into the reaction medium with heptane leads to a decrease in the yield of arenes to 23.0 mass %. At hexane transformation and its joint conversion with butane, hexane conversion is 78.6 % and 80.4 %, respectively.

The yield of isohexanes is found in a range of 53.2–55.4 mass %. An increase in the yield of hydrocarbon gases by 4.1 mass % also happens at joint conversion of butane and hexane. The content of aromatic hydrocarbons (see Fig. 4, b) at hexane conversion is 16.3 mass %, and the introduction of butane into the reaction medium leads to an increase in the yield of arenes to 20.4 mass %. There are no aromatic hydrocarbons at propane and butane conversion, as mentioned earlier, at this temperature.

According to catalytic tests results, one can note that the conjugation effect of the reactions is observed at conversion of hydrocarbons with different molecular mass.

Herewith, propane conversion in case of propane and heptane contributes to an increase in the yield of cracking products only, and at joint conversion of butane and hexane, the conjugation effect leads to both increasing the yield of cracking products, and aromatic hydrocarbons.

The kinetic parameters of the formation of hydrocarbons from hexane, heptane and binary mixtures of alkanes are presented in Table 1. Analysis of the data obtained demonstrates that the reaction rate constant (K_a) for heptane is $3.4 \cdot 10^{-2}$ s $^{-1}$, and at joint conversion of propane and heptane the value of K_a reduces almost twice to $1.9 \cdot 10^{-2}$ s $^{-1}$. A decrease in the aromatization selectivity to 0.5 in comparison with heptane conversion (0.6) is also observed for a mixture of C₃ + C₇. Unlike the previous pair of hydrocarbons, the conjugation effect at conversion of butane and hexane leads to an increase in K_a in 1.3 times from $1.9 \cdot 10^{-2}$ to $2.5 \cdot 10^{-2}$ s $^{-1}$. Additionally, an increase in the aromatization selectivity of butane, in comparison with hexane conversion from 0.4 to 0.5, is observed.

It follows from the dependence $\ln K_a$ on temperature ($1000/T$) presented in Fig. 5, a that the catalyst activity in the aromatization reac-

TABLE 1

Kinetic parameters of the formation of aromatic hydrocarbons

Characteristics	Heptane	Heptane + propane	Hexane	Hexane + butane
Reaction rate constant $K_a \cdot 10^{-2}$, s $^{-1}$ ($T = 773$ K)	3.4	1.9	1.9	2.5
Aromatization selectivity $S_a = K_a/K_o$ ($T = 773$ K)	0.6	0.5	0.4	0.5
Activation energy of the reaction (E_a), kJ/mol	50.0	140.6	90.7	80.1

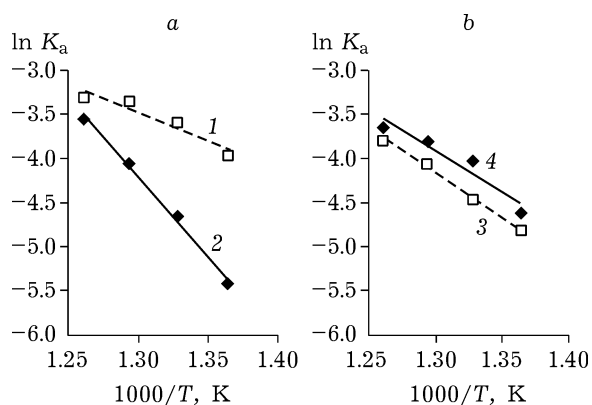


Fig. 5. Value of $\ln K_a$ vs temperature ($1000/T$, K): a - heptane (1), propane and heptane (2); b - hexane (3), butane and hexane (4).

tion in a region of the studied temperatures of 733–793 K ($1000/T = 1.36$ – 1.26) is significantly higher than at its joint conversion with propane. A different regularity is observed at hexane and butane conversion (see Fig. 5, b). It can be seen that the catalyst activity in the whole temperature range in aromatization of hexane and butane is higher than at hexane aromatization. Additionally, it should be noted that rate in heptane aromatization is higher than that of hexane.

The calculated value of the observable activation energy of the formation of aromatic hydrocarbons (E_a) from heptane is 50.0 kJ/mol (see Table 1), and the introduction of propane into the reaction medium leads to an increase of E_a in almost 3 times (140.6 kJ/mol). The totality of the results presented indicates that at conversion of a mixture of C₃ + C₇, propane hinders the joint aromatization reaction. At the introduction of butane in the reaction medium, a decrease in the observable activation energy of the formation of aromatic hydrocarbons at joint conversion of C₄ + C₆ to 80.1 kJ/mol, in comparison with E_a of hexane (90.7 kJ/mol), is observed, which indicates more favourable reaction conditions.

From these data, it follows that the major factor determining reactions of joint conversion of hydrocarbons is the nature of light alkane molecules. Since most likely precisely the activation of propane and butane molecules represents the rate limiting step of the reaction of the formation of aromatic hydrocarbons at joint conversion.

Heats of formation of carbocations at the break off of hydride ions from the propane and butane molecules are given in work [13].

It can be seen that the heat of formation of a primary cation for propane is 869 kJ/mol, its value for butane decreases to 844 kJ/mol. The values for the heats of secondary ion formation from propane is equal to 802 kJ/mol, and from butane – 765 kJ/mol. Additionally, if butane in the reaction medium is preliminary subjected to isomerization that yields to isobutane, the formation of a tertiary carbocation is possible. Herewith, the minimum value of heat equal to 706 kJ/mol is required to the break off of the hydride ion. From the data presented, it is evident that butane is more reactive due to lower energy expenditures required for performing the break off of the hydride ion.

Earlier in work [10], we suggested that joint conversion of butane and hexane proceeded on binary centres Pt^σ – L_z, where Pt^σ is electron deficient platinum with a charge of +2, and L_z is an acid Lewis site on the media. These centres possess bifunctional properties. Herewith, the activation of the butane molecule is carried out on L_z, while the hexane molecule is activated at a platinum centre (Pt^σ). The formation of aromatic hydrocarbons occurs from a single transition complex formed by two activated molecules. This explains effects of a decrease in the activation energy and an increase in the rate constant of the aromatization reaction in comparison with hexane conversion. It is obvious, in case of propane and heptane conversion, a single transition complex does not form, since a significant increase in the activation energy and the rate constant of aromatization in comparison with heptane conversion is observed. Apparently, the availability of a greater strength L_z is required for the activation of the propane molecule and its joint conversion with heptane into aromatic hydrocarbons. Despite this, the conjugation effect at the introduction of heptane into the reaction medium to the propane molecule is present and is reflected primarily in an increase in its conversion in comparison with individual transformation. However, the major reaction herewith represents cracking with the formation of methane and ethane.

CONCLUSION

Thus, the results obtained in the work testify the mutual effect of hydrocarbon in raw materials on major regularities of reaction behaviour. Alongside with that, one can state that conversion of hydrocarbon gases jointly with large molecular mass hydrocarbons has an obvious advantage in comparison with their individual conversion in a temperature range of 733–793 K. This advantage mainly consists in significantly lower energy costs required for the activation of an alkane molecule. However, if the catalytic Pt/Al₂O₃ system for butane apparently has sufficient strength and concentration of acceptor centres capable of the break off of the hydride ion followed by conversion of the activated molecule into aromatic hydrocarbons jointly with hexane, in case of propane, the strength and concentration of such centres are insufficient.

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