

The Use of C₂–C₅ Hydrocarbons for Production of Gasoline Components

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Abstract

A conversion of light hydrocarbons (C₂–C₅) over HZSM-zeolite-containing catalysts modified by the VA Group metals was studied. The process was carried out in a flow reactor at varying temperature from 350 to 400°C, pressure – 0.1-0.5 MPa and space velocity – 100-300 hr⁻¹. It was observed that catalysts had high activity in the process of interaction between pentane and ethylene at temperature 350-400°C and P = 0.1 MPa. The conversion of pentane and ethylene at these conditions over the catalyst P-3 are > 98% and 99-100% respectively. The reaction products are C₁–C₄ alkanes, C₃–C₄ alkenes and C₅⁺ hydrocarbons of normal and iso-structure, benzene, ethyl-benzene, xylene, toluene. Maximum yield of C₅–C₇ alkanes is 91.6% over P-2 and ethyl-benzene is 36.6% over P-3 catalyst observed at mild conditions T = 350°C and P = 0.1 MPa. Yield of benzene is 1.3-1.4% that meets to environmental requirements. The composition of alkylation gasoline depends on the catalyst nature. Studied zeolite-containing catalysts are polyfunctional and carry out the reactions of dehydrogenation, isomerization, cyclization, alkylation and partly cracking of hydrocarbons by one step. The process scheme is presented.

Introduction

The creation of the new catalytic technologies for the processing of gas condensate and casing-head gases is one of the main tendencies of gasoline components production.

Institut Français du Pétrole (IFP) developed and applies the processing of light hydrocarbons into the components of motor fuel or chemical products in industry [1]. These processes are based on the oligomerisation of olefins over solid catalysts in heterogeneous phase or over liquid ones in homogeneous phase depending on source used and desirable content of products obtained. Practically, all light hydrocarbons may be processed at the same set by using processes suggested by IFP. Thus, Polynaphtha process represents the oligomerisation of C₃–C₄ olefins allowing producing the motor spirit and jet engine fuel with a high quality due to using the heterogeneous catalyst [1]. Also, DIMERSOL processes are assigned for processing of light alkanes into gasoline and kerosene fractions.

In a number of works reviewed and analysed in [2-5] it was shown that C₆–C₈ arenes as well as aliphatic hydrocarbons of iso-structure are formed at catalytic conversion of light hydrocarbons over zeolite containing catalysts modified by various metals.

For the efficient use of propane-propylene fraction of catalytic cracking their conversion over the modified pentacyl-containing catalysts has been studied [6]. It has been shown that Zn-ZSMH-2 is the active and selective catalyst in the process of oligomerisation both of propylene and propylene-containing fractions. Depending on the nature of promoter introduced in the catalyst composition the selectivity on aromatic hydrocarbon production is changed. The promoter introduction has allowed developing the catalyst for conversion of propylene-containing fractions into gasoline components with high octane number or into concentrated aromatic products.

The technology for the production of alkylation gasoline as a component with high octane number is based on the use of the liquid mineral acids as a catalyst. This technology requires the high discharge intensity of both catalyst and electric energy and is environmentally dangerous.

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Therefore the process of paraffin alkylation by olefins is a topical problem. The main task is the transition from homogeneous catalysts (H₂SO₄, HF) to the effective heterogeneous ones. Because the last ones are more economically sound. Among the new heterogeneous catalysts the zeolite-containing poly-functional ones with more intensive acid properties as well as the complex systems containing the zirconium sulfite, metal oxides *etc.* [7] are of interest.

Experimental

The catalysts containing zeolite of HZSM type with ratio of SiO₂/Al₂O₃ = 27 and content of Na₂O < 0.1 mas.% were used. All catalysts include 45-48 mas.% of Al₂O₃ as a bonding agent as well as various additives. P-1, P-2, P-3 catalysts were prepared.

The samples were activated in air current at 550°C for 3 hours before experiments and then regenerated at 550°C for 2 hours. The catalyst loading was 2 cm³. The catalysts were tested in a flow reactor at pressure 0.1–0.5 MPa at varying temperature from 350 to 400°C and space velocity from 100 to 300 hr⁻¹. The experiment duration was about 1-2 hours.

The mix of pentane and ethylene was used as an initial source.

The analysis of gaseous and liquid catalysate was carried out by the chromatographic and IR-spectroscopy methods.

For determination of coke formation the thermogravimetric analysis was used (Q 1500D-derivatograph).

Results and Discussion

The interaction between pentane and ethylene begins to run actively at T=350°C. Light as well as liquid hydrocarbons are formed (Table 1 and Table 2).

The conversion degree of ethylene is in a region of 89.3–100% depending on the catalyst nature at T = 350–400°C. The ethylene conversion degree is 100% over P-1 and P-3 catalysts at 350°C and decreases to 99.7 and 99.9% respectively with temperature increase to 400°C. P-2 catalyst shows the lower activity. The degree of ethylene conversion is 89.3–91.4% over this catalyst at the same conditions (Table 1).

The degree of pentane conversion is varied from 35.6 to 98.7% that less than ethylene conversion at the same conditions. Catalyst P-2 shows the lowest activity in pentane conversion. The degree of pentane conversion is varied from 35.6 to 85% at tempe-

rate increase from 350 to 400°C. The high activity has been observed over P-3 catalyst, where the conversion degree of both reagents is higher than 98% at 350°C.

C₁–C₄- *n*- and iso-alkanes, C₃–C₄-olefins, including iso-butene and C₅+ *n*- and iso-alkanes are observed in the composition of light gaseous hydrocarbons formed at the alkylation of pentane with ethylene. The total yield of light hydrocarbons is dropped by the following order: 41.3→30.7→29.8% over P-1, P-2 and P-3 catalysts respectively at 350°C. With temperature growth to 400°C the total yield of light hydrocarbons decreases to 22.9–29.8%.

n- and iso-C₅–C₇-alkanes (1.3–91.6 mas.%), benzene (1.3–6.8%), toluene (4.0–35.3%), ethyl-benzene (3.1–36.6%), xylenes (4.5–10.8%) and C₈+ hydrocarbons (8.5–31.5 mas.%) are observed among liquid products. At 350°C the high yields of C₅–C₇-alkanes (91.6%) over P-2 catalyst and ethyl-benzene (36.6%) over P-3 catalyst have been produced. At these conditions almost equal quantities of tolyene (24.3%) and ethyl-benzene (27.5%) are formed at P-1 catalyst. It needed to notice that the content of benzene in reaction products is not high and is equal 1.3–1.6% at 350°C over P-2. It is important for production of eco-friendly gasoline (Table 2).

With pressure increase to 0.5 MPa at 400°C pentane conversion is increased to 97.0% and content of C₆+ hydrocarbons is 90.0%. Liquid catalysate has orange colour.

IR-analysis of liquid catalysate formed at T_{exp} = 350°C and P = 0.5 MPa showed the presence of the intensive absorption bands (*a.b.*) at 3030, 3000, 2950, 2900 and 2850 cm⁻¹ (Fig. 1). The adsorption bands at 3030 and 3000 cm⁻¹ are attached to CH-group at double bond, *a.b.* at 2950, 2900 and 2850 concern to CH-specie in CH₂–CH₃-groups of hydrocarbon chain. The intensive band at 1600 cm⁻¹ is characteristic for C=C-bond and the bands of medium intensity in a region of 2000–1700 cm⁻¹ are attached to mono-substituted aromatic ring. Also, the absorption bands corresponding to deformation vibration of CH-, CH₂- and CH₃-groups of hydrocarbon chain are observed. The appearance of bands in region of 800–600 cm⁻¹ confirms the presence of aromatic rings of benzene, toluene and xylene. Bands at 720–760 cm⁻¹ allow to suppose the presence of hydrocarbon chain of (CH₂)_n, where n > 6 without branching.

The varied composition of products formed at catalytic interaction of pentane with ethylene indicates on the complicated reaction mechanism. On the base

Table 1

Composition of gaseous reaction products at pentane + ethylene interaction over zeolite-containing catalysts
($S.V_{\text{ethylene}} = 100 \text{ hr}^{-1}$, $P = 0.1 \text{ MPa}$)*

Catalyst	$T_{\text{exp}}, ^\circ\text{C}$	Conversion of Ethylene, %	Content of gaseous products**, mas. %					
			Alkanes					$\text{C}_3\text{-C}_4$ olefins
			CH_4	C_2H_6	C_3H_8	C_4H_{10}	<i>n</i> - and iso- C_{5+}	
P-1	350	100	0.2	0.8	22.7	43.6	32.6	0.1
	400	99.9	0.7	4.5	30.1	43.9	19.7	1.0
P-2	350	89.3	0.2	1.4	12.2	12.8	56.7	6.0
	400	91.4	0.2	1.0	11.8	5.3	66.3	6.8
P-3	350	100	0.2	0.7	18.3	34.9	45.9	-
	400	99.7	0.9	4.4	32.5	45.2	15.9	0.8

Table 2

Composition of liquid reaction products at pentane + ethylene interaction over zeolite-containing catalysts
($S.V_{\text{ethylene}} = 100 \text{ hr}^{-1}$, $P = 0.1 \text{ MPa}$)*

Catalyst	$T_{\text{exp}}, ^\circ\text{C}$	Conversion of pentane, mas. %	Composition of liquid products, mas. %					
			<i>n</i> - and iso-alkanes $\text{C}_5\text{-C}_7$	Benzene	Toluene	Ethylbenzene	Xylene	C_{8+}
P-1	350	80.0	28.4	3.5	24.3	27.5	7.8	8.5
	400	77.8	36.9	3.0	15.1	24.1	10.8	10.1
P-2	350	35.6	91.6	1.3	4.0	3.1	-	-
	400	85.0	28.0	1.6	12.0	22.4	4.5	31.5
P-3	350	98.7	1.3	1.4	23.0	36.6	9.2	28.5
	400	98.3	1.7	6.8	35.3	29.8	10.6	15.8

*Yield of gaseous and liquid products was separately calculated on the assumption of 100% of each phase

** Hydrogen was observed in trace amount

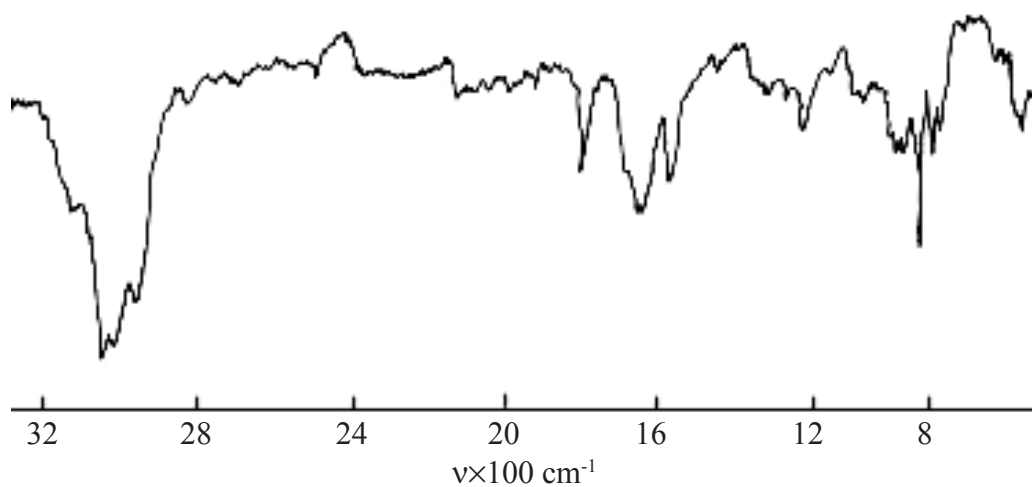
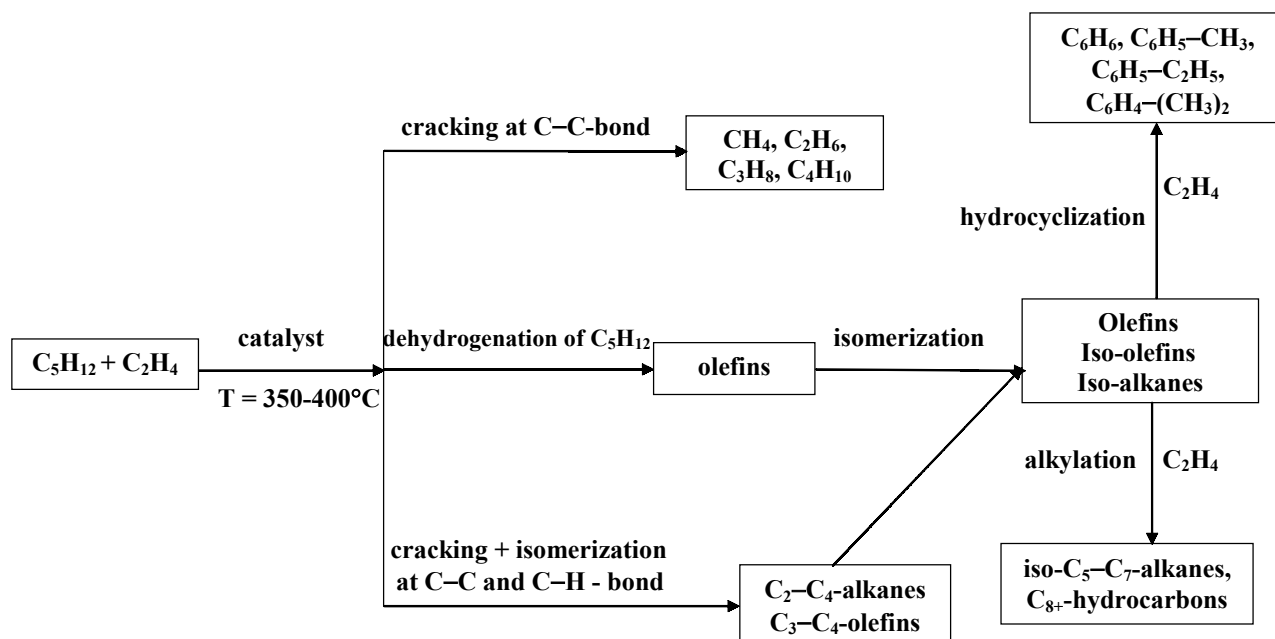


Fig. 1. The IR-spectra of liquid catalysate.

of GC- and IR-spectroscopic analysis the following mechanism is suggested (Scheme 1). There are four

main directions of the combined conversion of pentane and ethylene.



Scheme 1

Pentane is exposed to dehydrogenation with olefin formation and following isomerization into iso-olefins and iso-alkanes over the certain centers.

Iso-alkanes interact with ethylene with formation of iso-C₅–C₇-alkanes.

Alkenes participate in hydro-cyclization with formation of aromatics such as toluene, ethyl-benzene and xylene over the certain centers.

Pentane is exposed to cracking C–C- and C–H-bonds with formation of CH₄, C₂–C₄-alkanes and C₃–C₄-olefins. In further olefins participate in the processes of isomerization, hydrocyclization and hydrogenation to *n*- and iso-C₄-alkanes.

Conclusions

Polyfunctional catalysts on the base of zeolites having the high activity in the reaction of interaction of pentane with ethylene with formation of gasoline are developed. Gasoline composition is varied depending on the catalyst nature.

It is shown that at presence of P-3 polyfunctional zeolite-containing catalyst the liquid product containing of petrol components is formed at the interaction between pentane and ethylene at 350-400°C. The maximum degree of pentane conversion is 98.7% and

ethylene – 100%.

Polyfunctional catalysts carry out dehydrogenation, isomerization, alkylation, hydrocyclization and partially cracking. The product composition is an evidence of that.

The specific of developed process is low temperature and pressure as well as high conversion of initial reagents.

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