

## Alkylating Activity of an Omnikat-210P Zeolite Catalyst Modified with Ni, Cr, and Co

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**Abstract**—An Omnikat-210P zeolite catalyst modified with Ni, Cr, and Co in a total amount of 4.53 wt % has been synthesized. X-ray diffraction analysis of the catalyst has been conducted; the oxide content of the original and modified catalyst has been determined. The dependence of the liquid yield on reaction temperature, contact time, and feed space velocity has been revealed. It has been found that the reaction products comprise 49.1 wt % isoparaffins and 41.3 wt % aromatics with no olefin hydrocarbons. The boiling range of the liquid products is 27.9–253.7°C. The octane number of the liquid products is on the order of RON 90.7.

**Keywords:** zeolite catalyst, catalytic cracker gases, alkylation, olefins, paraffins, contact time, temperature, isoparaffins

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Improvement of internal combustion engines and tightening of the environmental requirements for gasoline dictate the need for high-octane motor fuel components. The development of novel methods for the production of high-octane components, in particular processes involving alternative raw materials, is of considerable interest [3, 4]. Thus, the complex processing of all hydrocarbon components of refinery gases will lead to a decrease in the consumption of nonrenewable natural resources and the production of valuable chemicals.

The average total yield of hydrocarbon gases at refineries is 4–8 wt % of the amount of crude oil [5, 6]. The C<sub>3</sub>–C<sub>4</sub> hydrocarbon fractions in petroleum refining are a mixture of normal paraffins, isoparaffins, and olefins. It is of fundamental importance that these fractions are used to produce a high-quality gasoline conforming to international European standards, which limit the aromatics content in automotive gasoline to 30%; in particular, the benzene content should be less than 1% [7, 8].

The main condition for the organization of the integrated processing of hydrocarbon gases at refineries is the development of the most efficient technological solution [9], namely, the conversion of these gases to liquid hydrocarbons, for example, high-octane gasoline additives. The commercial processes commonly used for the production of these additives include oligomerization, isomerization of the propane–propylene (PP) and butane–butylene (BB) fractions (Dimersol-G), and isobutane alkylation with olefins [10]. The alkylation reaction results in the coconver-

sion of isobutane and butylenes to form gasoline fractions containing mostly isooctanes with a high octane numbers (ON).

The most promising line in the development of alkylbenzene production is the use of zeolite catalysts whose specific properties (particular microporous structure, acidity) and technical and economic parameters make it competitive with conventional commercial catalysts, such as H<sub>2</sub>SO<sub>4</sub> and HF. In addition, zeolite catalysts do not exhibit corrosive activity; they most fully meet the environmental standards [11].

The aim of this study is to convert catalytic cracker gases to high-octane liquid products without separation into PP and BB fractions and determine the effect of contact time, temperature, and feed space velocity on the liquid yield.

### EXPERIMENTAL

An Omnikat-210P commercial zeolite catalyst modified with Ni, Cr, and Co in a total amount of 4.53 wt % was used. The Ni, Cr, and Co metals were deposited on the zeolite catalyst in amounts of 1.53, 1.48, and 1.52 wt %, respectively, using Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, and Cr(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O metal nitrates. The Omnikat-210P catalyst was preground using a Retsch PM 100 mill for 12 h. The original catalyst has a particle size of 65–70 μm and a bulk density of 0.61–0.65 g/cm<sup>3</sup>. After grinding, the particle size decreased to 5–10 μm and the bulk density increased to 1.00 g/cm<sup>3</sup>. The binder for the ground particles was γ-Al<sub>2</sub>O<sub>3</sub>. After the deposition of cobalt, nickel, and

**Table 1.** Chemical composition of the catalysts

	Concentration in catalysts, wt %	
	original	modified
SiO <sub>2</sub>	44.9	39.9
Al <sub>2</sub> O <sub>3</sub>	45.6	40.3
Fe <sub>2</sub> O <sub>3</sub>	1.42	1.35
REE oxides	3.445	2.916
TiO <sub>2</sub>	3.02	2.33
MgO	0.755	—
Cl	0.5	—
SO <sub>3</sub>	0.36	—
CoO	—	3.91
Cr <sub>2</sub> O <sub>3</sub>	—	4.08
NiO	—	4.59

chromium nitrates, the catalyst was shaped into beads of 3–4 mm in diameter, dried (120°C), and calcined (450–500°C) in a vacuum at a residual pressure of 10–15 mmHg.

The concentration of the main components in the original and modified catalysts is listed in Table 1.

Catalytic tests on the conversion of hydrocarbons contained in the catalytic cracker gases were conducted in a fixed-bed isothermal flow reactor at a temperature of 250–300°C, a feed space velocity of 30–260 h<sup>-1</sup>, and a catalyst charge of 164 cm<sup>3</sup>.

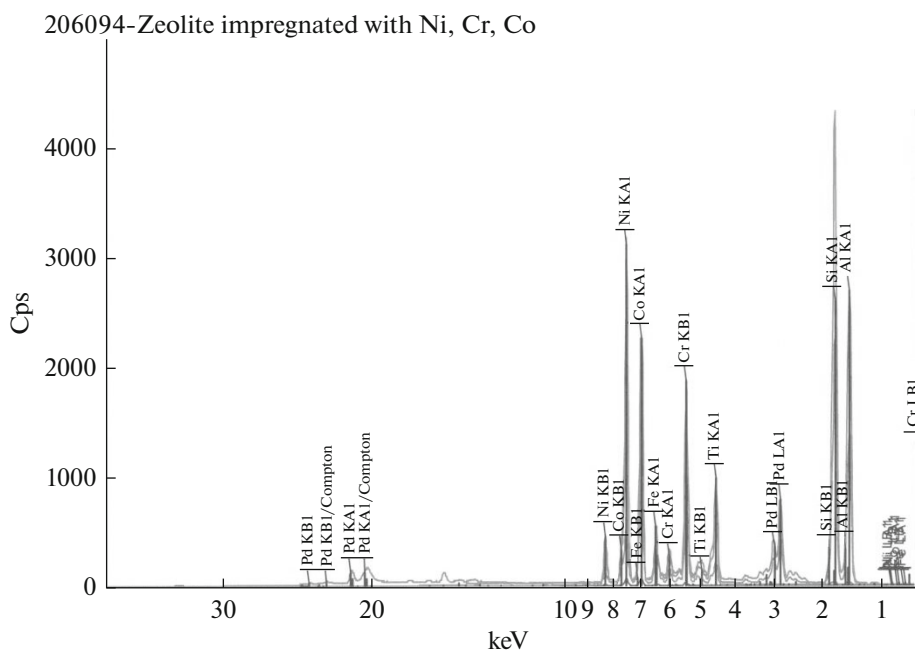
X-ray diffraction studies of the original Omnikat-210P zeolite catalyst and the catalyst modified with Ni, Co, and Cr (Fig. 1) were conducted on a PANalytical X'Pert Powder diffractometer (the Netherlands).

The feedstock was catalytic cracker gases; their composition is given in Table 2. The composition of the feedstock and the contact gas was assessed using an LKhM-8MD chromatograph (3 mm × 3.5 m column; sample size, 0.5 cm<sup>3</sup>; carrier gas (helium) inlet pressure, 2 atm; evaporator temperature, 20°C; column temperature, 30°C; detector port temperature, 20°C; detector current, 150–160 μA; and recorder chart speed, 720 mm/h). The hydrocarbons were separated using triethylene glycol di-*n*-butyrate (TEGB) as a stationary phase.

Liquid products were analyzed on a PerkinElmer Auto System gas chromatograph interfaced to an XL\_DHAX (Detailed Hydrocarbon Analysis Extended) mass selective detector by the PONA method using polyvinyl siloxane as a liquid stationary phase; helium as the carrier gas at linear velocity of 24 cm/s; sample volume, 0.5 μL; column length, 100 m; column diameter, 0.25 mm; and column temperature programming, (5–48)–(141–300)°C.

The composition of the liquid products obtained in the conversion of hydrocarbons contained in the catalytic cracker gases is shown in Table 3.

Table 4 shows the percent boiling point properties of the liquid products.

**Fig. 1.** X-ray diffraction pattern of the Omnikat-210P zeolite catalyst modified with Ni, Co, and Cr.

**Table 2.** Feedstock composition

Unit of measure	$\Sigma C_2$	$C_3H_8$	$C_3H_6$	$i-C_4H_{10}$	$n-C_4H_{10}$	$\alpha C_4H_8$	$i-C_4H_8$	$cis-C_4H_8$	$trans-C_4H_8$	$n-C_5H_{12}$	$\Sigma$
vol %	0.33	19.45	50.77	15.39	3.33	3.17	2.5	3.17	1.83	0.06	100

## RESULTS AND DISCUSSION

Figure 2 shows the effect of contact time on the liquid yield. In this case, the amount of olefinic and paraffinic hydrocarbons per unit weight of catalyst decreases (from 0.1956 to 0.1235 g/g cat and from 0.1389 to 0.078 g/g cat, respectively). At a contact time of 42 s, the amount of paraffins in the feedstock per gram of catalyst decreases by 43.8% compared with the paraffin content in the feedstock at a contact time of 23.5 s; however, the liquid yield on feed basis increases by 25% and achieves a level of 82%. With an increase in the contact time from 23.5 to 42 s, the liquid yield on total olefins basis and total paraffins basis in the feedstock increases by 1.3 and 13.8%, respectively. Hence, the conversion of paraffins is higher; this means that *n*-paraffins are also involved in alkylation. An increase in the catalyst activity in paraffin dehydrogenation provides a significant increase in the olefin content, which in turn, provides the occurrence of the paraffin alkylation reaction (Fig. 2).

The effect of reaction temperature (260–300°C) on the liquid yield was studied. Figure 3 shows that the liquid yield per gram of catalyst increases from 0.083 to 0.1675 g with an increase in temperature from 260 to 300°C. The liquid yield on total feedstock paraffins basis increases from 0.037 to 0.078 g/g cat; the olefin content in the feedstock is 0.048–0.1235 g/g cat. However, in terms of change in the liquid yield per each 10°C, the yield decreases from 13.4 to 7.1% and from 14.7 to 7.3% per total feedstock  $C_3$ – $C_4$  olefins and  $C_3$ – $C_4$  paraffins, respectively. The liquid yield per initial fraction increases from 48.2% (260°C) to 82% (300°C). In terms of liquid products per each 10°C, the liquid yield reaches a maximum value of 22% at a temperature of 280°C and then decreases to 4.9% at a temperature of 300°C.

**Table 3.** Composition of the liquid products

Hydrocarbons	wt %	vol %
Paraffins	2.32	2.3
Isoparaffins	49.13	55.98
Olefins	0.00	0.00
Naphthenes	2.95	2.84
Aromatics	41.3	34.7
$\Sigma C_{14}$ and higher	4.3	4.18
Total	100	100

As the temperature increases (from 260 to 300°C), the liquid yield per paraffinic and olefinic hydrocarbons in the feedstock increases by a factor of 2.21 and 2.76, respectively. The liquid yield on feed basis increases by 70.1% (Fig. 3).

An increase in the liquid yield with the increasing temperature is attributed to the occurrence of dehydrogenation of paraffins to olefins, isomerization of *n*-paraffins to isoparaffins, and dehydrocyclization of paraffin hydrocarbons.

Figure 4 shows the variation in the liquid yield (on feed basis) as a function of temperature (260–420°C) and feed space velocity (30–260 h<sup>-1</sup>).

It is evident from Fig. 4 that the highest liquid yield at each of the temperatures is achieved at a feed space velocity of 150 h<sup>-1</sup>. At temperatures of 260 and 300°C, the liquid yields are ~86 and ~80%, respectively; at 420°C, the liquid yield decreases compared with that at 300 and 260°C. At a temperature of 420°C, the residence time of olefinic and paraffinic hydrocarbons on the catalyst surface is extremely short; therefore, they are desorbed from the surface without undergoing alkylation.

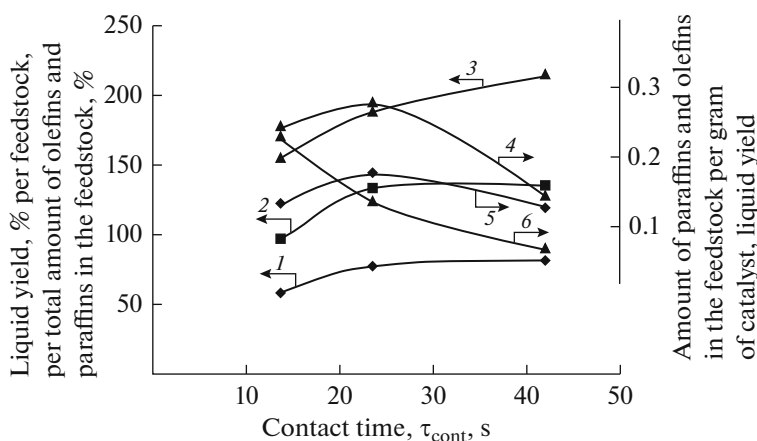
Thus, the study has revealed that the conversion of  $C_3$ – $C_4$  paraffinic hydrocarbons contained in the catalytic cracker gases over the Omnikat-210P zeolite catalyst modified with Ni, Co, and Cr leads to the formation of liquid alkylates. The composition of the liquid products has been determined: the products comprise 49.1 wt % of isoparaffins, whereas olefinic hydrocarbons are completely absent. The RON of the liquid reaction products is on the order of 90.7.

The study of the effect of temperature (260–300°C) on the liquid yield has revealed that the highest increase in the liquid yield per each 10°C—by 22%—is observed at 280°C.

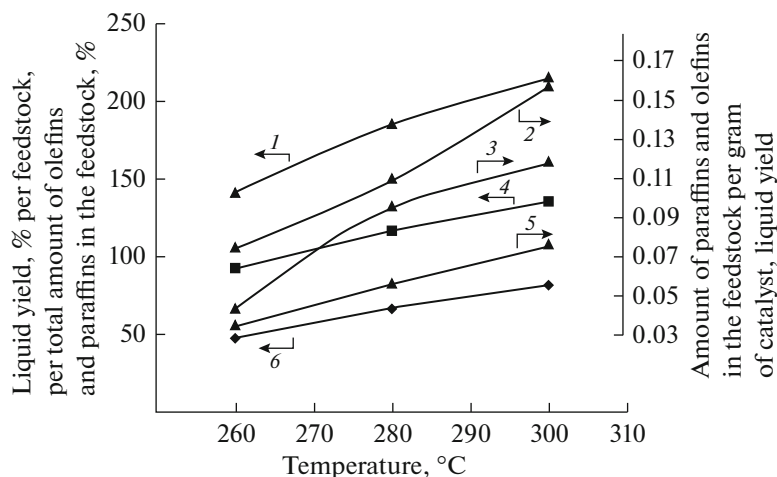
The study of the effect of contact time (23.5–42 s) on the liquid yield has revealed that an increase in the contact time leads to a 5% increase in the liquid yield (by 1.3 and 13.9% on total  $C_3$ – $C_4$  olefins and  $C_3$ – $C_4$  paraffins, respectively). Hence, in the presence of a modified zeolite catalyst, paraffins undergo dehydro-

**Table 4.** Boiling point properties of the liquid product

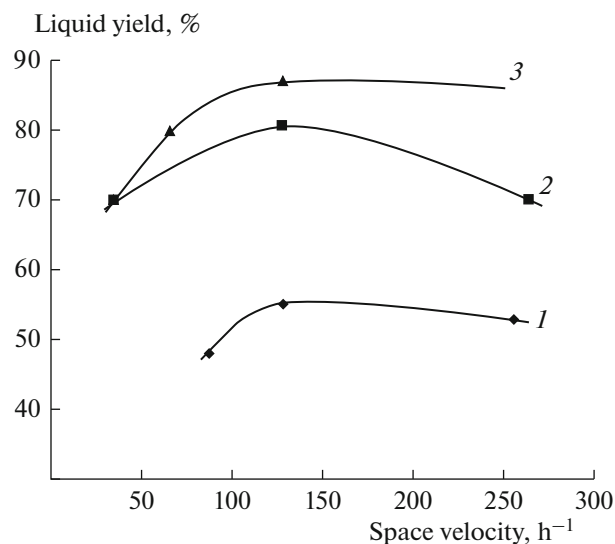
Percentage distilled, %	IBP	10	50	90	EBP
Temperature, °C	27.9	27.9	87.9	142.5	253.7



**Fig. 2.** Variation in the liquid yield as a function of contact time: (1) liquid yield on feed basis, wt %; (2) liquid yield total feed  $C_3$ – $C_4$  olefins basis, wt %; (3) liquid yield on total feed  $C_3$ – $C_4$  paraffins basis, wt %; (4) liquid yield per gram of catalyst, g/g cat; (5) amount of  $C_3$ – $C_4$  olefins in the feedstock per gram of catalyst, g/g cat; and (6) amount of  $C_3$ – $C_4$  paraffins in the feedstock per gram of catalyst, g/g cat.



**Fig. 3.** Variation in the liquid yield as a function of temperature: (1) liquid yield on total feed  $C_3$ – $C_4$  paraffins basis, wt %; (2) liquid yield per gram of catalyst, g/g cat; (3) amount of  $C_3$ – $C_4$  olefins in the feedstock per gram of catalyst, g/g cat; (4) liquid yield on total feed  $C_3$ – $C_4$  olefins basis, wt %; (5) amount of  $C_3$ – $C_4$  paraffins in the feedstock per gram of catalyst, g/g cat; and (6) liquid yield per feedstock, wt %.



**Fig. 4.** Variation in the liquid yield as a function of feed space velocity and temperature: (1) 420, (2) 300, and (3) 260°C.

generation to olefinic hydrocarbons, which are subsequently involved in alkylation.

The study of the effect of feed space velocity (30–260 h<sup>-1</sup>) on the liquid yield has revealed that the highest liquid yield is achieved at a feed space velocity of 150 h<sup>-1</sup>.

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