

REFORMING OF *n*-HEXADECANE ON MODIFIED ALUMINOSILICATES

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Catalysts containing amorphous aluminosilicate and crystalline zeolite phases are widely used for industrial cracking of petroleum cuts. These catalysts also exhibit high activity in cracking of individual hydrocarbons.

The activity and selectivity of the amorphous aluminosilicate phase can be increased by modifying it with metal oxides, creating additional ensembles of tetrahedrons of the type $(\text{AlO}_4 \cdot \text{SiO}_4 \cdot \text{MeO}_4)$ or ensembles of polyhedrons of another composition: $(\text{AlO}_6 \cdot \text{SiO}_4 \cdot \text{MeO}_4)$ or $(\text{AlO}_4 \cdot \text{SiO}_4 \cdot \text{MeO}_6)$ in the lattice. These ensembles are randomly positioned in the lattice, which also reflects the amorphous structure of metal silicates.

In special conditions – in liquid medium (water) at high pressure, metal silicates crystallize with formation of zeolites. When incorporated in the amorphous phase, zeolites serve as active catalytic components.

Cobalt or zirconium compounds which also attack the aluminosilicate structure, changing the activity and selectivity of the catalysts, can also be added to the amorphous phase. New data on the activity of metal aluminosilicate catalysts containing these compounds in a fixed amount are reported here. The catalysts were

Table 1

Catalyst (arbitrary designation)	pH of sol in synthesis	Chemical composition,* wt. %			
		SiO ₂	Al ₂ O ₃	CaO	ZrO ₂
K ₁	10.5	92	–	7.84	–
K ₂	4.5	92.2	–	7.74	–
K ₃	4.5	89.75	8.5	1.22	–
K ₄	10.5	90.8	6.97	1.38	–
K ₅	10.5	87.7	9.06	–	2.18
K ₆	4.5	86.9	11	–	1.38

Note. * Remainder – sodium oxide

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Table 2

Compound	Unit cell size, nm		
	a	b	c
Co ₂ SiO ₄	0.4781	1.0296	0.5998
CoSiO ₂	1.8296	0.8923	0.5204

Table 3

Catalyst (see Table 1)	Pore volume (cm ³ /g) after heating at, °C			Average pore radius (nm) after heating at, °C		
	500	700	900	500	700	900
K ₁	0.63	0.51	0.46	0.832	0.904	1.312
K ₂	0.64	0.55	0.23	0.447	0.954	1.162
K ₃	0.24	0.14	0.05	0.910	0.900	1.020
K ₄	0.65	0.47	0.19	0.388	0.821	1.594
K ₅	0.29	0.16	0.13	1.450	2.250	4.090
K ₆	0.24	0.17	0.16	1.970	2.430	4.300

used for conversion of *n*-hexadecane to reveal the basic types of reactions (cracking, reforming, isomerization, etc.) that determine the composition of the catalyzate and hydrocarbon gases.

Aluminosilicate catalysts modified with cobalt and zirconium compounds were synthesized in a continuous unit by feeding aqueous solutions of Al₂(SO₄)·18H₂O, Co(NO₃)₂·8H₂O, and ZrOCl·8H₂O salts and an aqueous solution of liquid glass, Na₂SiO₃, in the corresponding ratios, in the mixing unit. In mixing the solutions at 10°C and pH 4.5 or 10.5 (to establish the effect of the pH on the properties and activity of the catalyst), a metal aluminosilicate sol was obtained.

The sol stream in the form of microdrops was passed through a grooved divider into a lower container filled with transformer oil. In passing from the surface of the oil to the bottom of the vessel, the sol droplets solidified into gel beads. The beads formed were placed in a separate container, washed with distilled water, and underwent syneresis for 8 h at 40°C in the mother liquor separated from them. The mother liquor was displaced from the container with an activating aqueous solution of (NH₄)₂SO₄ and the gel was activated at 50°C for 24 h. Substitution of Na⁺ ions by NH₄⁺ ions took place in bulk and on the surface of the hydrogel particles in activation. Activation continued until the Na⁺ ions were totally substituted, determined by the absence of these ions in the hydrogel particles.

The activated hydrogel was washed with distilled water until the SO₄²⁻ ions in the washing water totally disappeared. The gel was separated from the moisture on a filter, placed in an oven, and dried at 110°C to a constant weight, then calcined in an air stream at 500, 700, and 900°C for 6 h.

After calcination, the catalysts were stored in a desiccator to prevent sorption of moisture and organic compounds from the environment. The chemical composition was determined, the IR and x-ray structural spectra were recorded, and the acidity, external appearance, specific surface area, volume, and average pore radius were determined for the catalysts calcined at 500°C.

The chemical composition and acidity of the external surface of the modified catalysts are reported in Table 1. The basic components are SiO₂ and Al₂O₃, CoO, and ZrO₂, which play the role of modifiers.

The x-ray structural analysis showed that the modified and initial aluminosilicates are x-ray amorphous structures, while the cobalt silicate has a crystal lattice with an orthorhombic unit cell whose size is shown in Table 2 for the two compounds identified.

Table 4

Catalyst (see Table 1)	Specific surface area (m ² /g) after heating at, °C		
	500	700	900
K ₁	151	113	56
K ₂	271	260	151
K ₃	228	113	99
K ₄	335	295	67
K ₅	253	194	166
K ₆	246	168	161

Table 5

Catalyst (see Table 1)	Acidity (meq H ⁺ /g) after heating at, °C		
	500	700	900
K ₁	2.45	2.35	2.3
K ₂	3.76	2.7	2.35
K ₃	4.8	2.85	2.75
K ₄	2.8	2.4	2.2
K ₅	3.45	2.3	2.15
K ₆	3.8	2.8	2.4

The absorption bands at 730-780 cm⁻¹ in the IR spectra of the modified aluminosilicates were assigned to vibrations of the bonds in island ensembles of {AlO₄Table 3·SiO₄} tetrahedrons, those at 500-600 cm⁻¹ were assigned to polymerization ensembles of {MeO₆·SiO₄} tetrahedrons, those at 1600-1700 cm⁻¹ to hydroxylated >AlO₆H·SiO₄} polyhedrons, and those at 3452 cm⁻¹ to hydrated silicon oxide tetrahedrons {SiO₄·SiO₄}H₂O.

The texture of the catalysts was determined by adsorption of nitrogen. The average radius and pore volume characterizing it are reported in Table 3. The pore volume decreased and the average radius increased when the sample heating temperature increased from 500 to 900°C. The increase in the average radius is due to destruction of blind pores joined by narrow pores into wider pores due to the effect of water vapor and a decrease in the number of winding pores. These three causes of the change in texture reflect an overall change in the physical properties of the catalysts. The wider-pore catalysts were synthesized in basic medium.

The calculated specific surface areas of the investigated catalysts are reported in Table 4. Catalyst K₄, synthesized at pH 10.5, has a higher specific surface area than the other catalysts. The specific surface area of the catalysts decreased with an increase in the calcination temperature as a result of an increase in the average pore radius.

The acidity was investigated by titration of suspensions of the samples in benzene with a solution of *n*-butylamine to determine the nature of the activity of the modified catalysts in reforming and cracking of *n*-hexadecane. The acidity of the accessible active ensembles of tetrahedrons containing or not containing hydroxyl groups was determined in titration. The results of the experiments are reported in Table 5.

Catalysts K₂, K₃, and K₆, synthesized from sol at pH 4.5, had higher acidity. Moreover, their specific surface was lower than for catalysts K₁, K₄, and K₅, synthesized at pH 10.5. As a consequence, the activity of the catalysts is not directly correlated with the acidity of their surface. It can be explained by the premises of the theory of catalysis by polyhedrons in [1, 2].

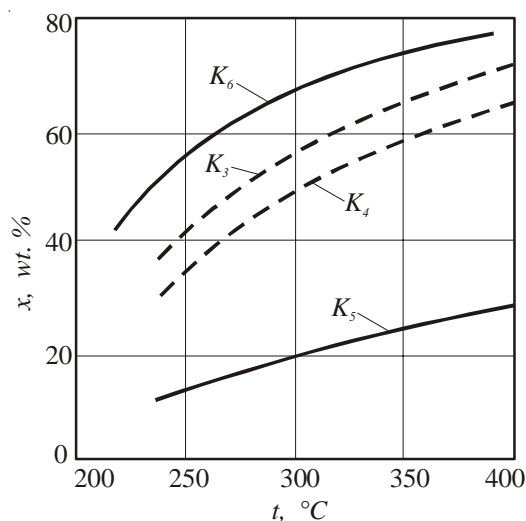


Fig. 1. Degree of conversion x of n -hexadecane vs. temperature t on catalysts modified with zirconium oxide (solid curves) and cobalt oxide (dashed curves).

According to this theory, amorphous lattices with a higher content of ensembles of tetrahedrons of the $\{\text{AlO}_4 \cdot \text{SiO}_4\}$, $\{\text{SiO}_4 \cdot \text{ZrO}_4 \cdot \text{AlO}_4\}$, $\{\text{SiO}_4 \cdot \text{AlO}_4 \cdot \text{SiO}_4\}$, and $\{\text{CoO}_{43} \cdot \text{SiO}_4 \cdot \text{AlO}_4\}$ type are obtained from the sol in acid medium. This is confirmed by the IR spectra of the catalysts synthesized from sols at pH 4.5 and 10.5.

After the physicochemical properties, composition, structure, and acidity of catalysts K_1 - K_6 , their activity in cracking and reforming of liquid n -hexadecane was investigated. The reactions were conducted in a continuous unit in the gas phase in conditions of ideal displacement of the vapor phase over the catalyst bed. The reactor was charged with 40 cm³ of bead or grain catalyst, and it was heated in a stream of dried air with impurities removed at 500°C for 3 h.

Conversion of n -hexadecane took place in the 350-400°C temperature range at a feed rate of 1 cm³/(cm³·h) for 1 h. At the end of the process, the degree of conversion of the feedstock and content of four classes of hydrocarbons in the catalyzate: paraffins, olefins, naphthenes, and aromatics, were determined.

The increase in the degree of conversion with an increase in the temperature in the catalyst bed (Fig. 1) is due to both activation of the hydrocarbon molecules in the feedstock and to electron promotion (or electron respiration) of tetrahedron ensembles. Catalysts K_3 and K_5 synthesized at pH 4.5 and modified with cobalt and zirconium compounds exhibited high acidity and consequently higher activity.

Catalyzate was obtained on catalyst K_6 that distills within 30-165°C and has the following hydrocarbon composition, wt. %: 10.05 n -paraffins; 9.21 olefins; 18.50 naphthenes; 38.12 isoparaffins; and 23.49 aromatics. The octane number (motor) of the catalyzate was 79.3.

Based on these data, we note that the n -hexadecane molecules undergo cracking and reforming reactions in the presence of the zirconium aluminosilicate catalyst. The yield of gaseous hydrocarbons increased from 0.9 to 4.5 wt. % with an increase in the temperature. The presence of C_1 - C_{15} hydrocarbons in the products of conversion indicate catalytic cracking processes.

Hexadecane is present in the catalyzate both in the initial and in isomeric forms. Unsaturated hydrocarbons and aromatics – benzene and alkylbenzenes with a shorter alkyl radical – are formed in cracking reactions.

The presence of isoparaffins, naphthenes, and aromatic hydrocarbons in the catalyzate indicates reforming of n -hexadecane. Isoparaffins are formed by isomerization of n -paraffins on ensembles of tetrahedrons.

Reactions of dehydrocyclization of molecules of unsaturated hydrocarbons take place on the same ensembles with formation of aromatics. Naphthenes can be synthesized in several reactions: Diels–Adler,

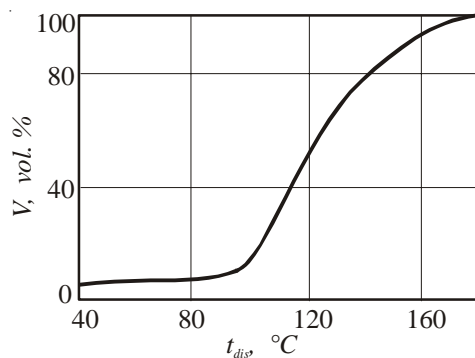


Fig. 2. Curve of distillation of liquid reformate into narrow cuts (V , t_{dis} – distillation volume and temperature).

cyclization of olefins with formation of cyclohexane and decalin, whose dehydrogenation yields benzene and naphthalene, respectively.

This approach to explaining the chemistry of conversion of *n*-hexadecane on modified aluminosilicate catalysts, i.e., with separation of cracking and reforming processes, will allow more clearly elucidating the quality of the catalyzate obtained.

The liquid catalyzate was distilled from an Engler flask into narrow cuts to determine its motor properties. The distillation curve obtained (Fig. 2) is characteristic of the commercial naphtha cut, 50 vol. % of which distills at a temperature no higher than 120°C. As a consequence, a high-octane component as an additional additive for commercial gasoline can be obtained in conversion of *n*-paraffins in low-octane naphtha cuts on cobalt- and zirconium-modified aluminosilicate catalysts.

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