

Cracking of C₃-C₄ Hydrocarbons on Cobalt and Palladium-Carbon Catalysts

G.E. Sataeva¹, R.M. Mansurova^{1*}, N.F. Toktabaeva², N.M. Rahova¹.

¹Al – Farabi Kazakh State National University. 480012, Almaty, 95, Karasai Batyr Str., Kazakhstan.

²D.V.Sokolsky Institute of Organic Catalysis and Electrochemistry,

142 Kunaev St., 480100 Almaty, Kazakhstan

Abstract

The process of C₃-C₄ hydrocarbon cracking on cobalt and palladium carbonic catalysts, obtained under conditions of propane-butane mixture pyrolysis, was studied. It was found that using of carbon-mineral catalyst increases gas conversion and selectivity, yield of olefines and aromatic compounds.

Introduction

The problem of utilization of exhausted gases from petroleum refining and petroleum chemistry industries and also of natural gas stimulates the search of new catalysts of C₃-C₄ hydrocarbon conversion. In the work [1] it is stated that in the presence of new catalytic systems-zeolite, promoted by cobalt (3%), C₃-C₄ hydrocarbons can be converted to a mixture of C₆-C₉ (and higher) aromatic hydrocarbons.

In the work [2] new metal-carbonic catalysts and fields of their using in catalytic reactions of CO and carbon conversion are studied. Study of reaction of C₃-C₄ hydrocarbon cracking on cobalt and palladium-carbonic catalysts is of interest.

Aim of this work is to obtain cobalt and palladium-carbonic catalysts, obtained by soaking of Narynkol clay by solutions of cobalt and palladium salts, and overcarbonized under conditions of propane-butane mixture pyrolysis and to test catalysts obtained in C₃-C₄ hydrocarbon reactions.

Experimental

The process of formation of catalytic carbon on catalyst during cracking and cracking of propane-butane mixture on overcarbonized nickel mineral catalysts were studied before [3,4]. Carbomineral cobalt and palladium catalysts were obtained by methodics, worked out in the laboratory of hybrid tech-

nologies of Combustion Problem Institute [5-7] on a flowing apparatus at 550 – 800 °C temperature interval and flow rate of propane-butane mixture 80-90 cm³/min. Prepared by extrusion on granulator clay was dried at room temperature, then held in muffle at 800 °C for 2 hours, then cooled down on the air to room temperature. Obtained by this way granules were used in further work.

The experiments on the study of carbon conversion process were carried out in a flowing quartz reactor at temperatures 500-740 °C, feed rate W=1000 h⁻¹ in flow of hydrogen [8]. Overcarbonized Narynkol clay, promoted by cobalt or palladium (3%) was used as catalysts. Liquid and gaseous products of reaction of C₃-C₄ carbon cracking were analysed by chromatographic method.

Results and Discussion

Cobalt - carbon catalysts obtaining process was studied by method of microdiffraction and it shows the picture is represented by three rings with interplanar distances d₁= 3,63 Å; d₂=2,24 Å; d₃=1,84 Å; corresponding to cobalt. Cobalt particles reach 200 Å, and cobalt is hexahedron. (Fig.1-electronic-microscopic shot).

On the electronic-microscopic shots overcarbonised at 650 °C clay is represented by threadlike -tubular semitransparent formations of different size and elasticity. Semitransparent formations fall under mica. In overcarbonized at 700 °C clay besides threadlike-tu-

*corresponding author. E-mail: mansurov@lorton.com

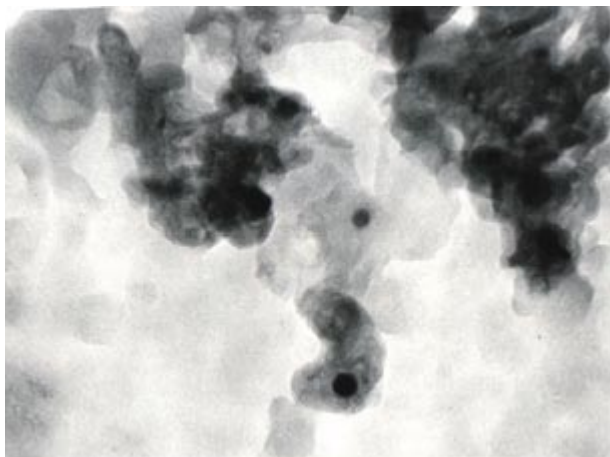


Fig.1. Overcarbonized cobalt catalyst. (Enlargement 160000). $d = 200 \text{ \AA}$

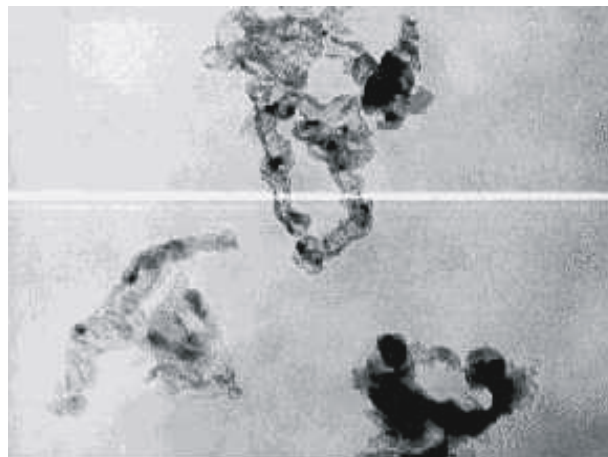


Fig.3. Overcarbonized cobalt containing catalyst. (Enlargement 120000). $d = 300 \text{ \AA}$

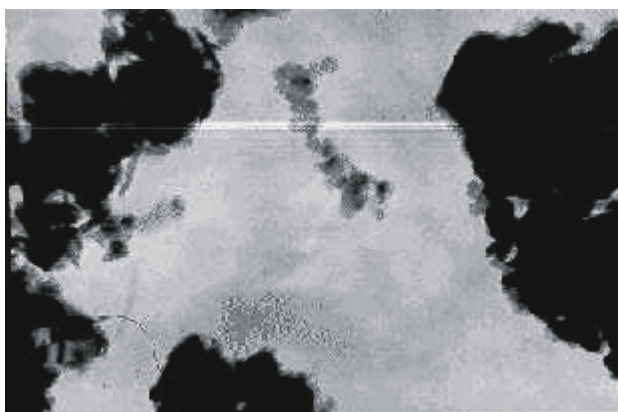


Fig.2. Overcarbonized clay. (Enlargement 120000). $d = 200\text{-}300 \text{ \AA}$

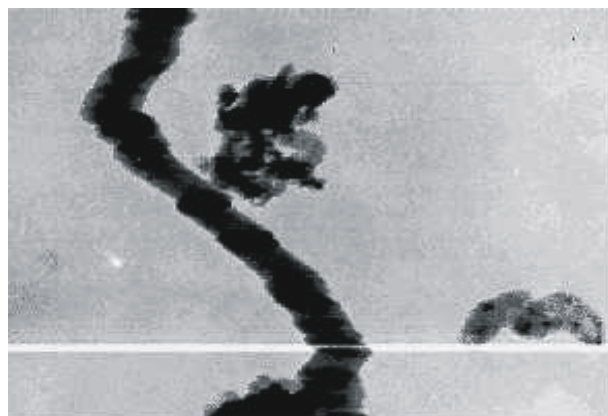


Fig.4. Overcarbonized cobalt containing catalyst. (Enlargement 120000). $d = 600 \text{ \AA}$

bular formations there are formations of tape type for which linear intergrowth of crystals is typical. Size of the particles $200\text{-}300 \text{ \AA}$ (Fig. 2).

Fig. 3,4 show overcarbonized cobalt catalysts, which are non-uniform interrupted tubes with diameter more than 300 \AA at $750 \text{ }^\circ\text{C}$. At $800 \text{ }^\circ\text{C}$ there are dense tapes of graphite type, tube diameters are more than 600 \AA , enlargement - 120000.

Results of chromatographic analysis of products of C₃-C₄ hydrocarbon conversion are shown in Table 1,2 and Fig 5-7. Obtained results show that products of reaction are olefines. (ethylene, propylene, iso-propylene), aromatic compounds (benzene, toluene, ethylbenzene, xylene) and also hydrogen, methane, ethane, propane, butane, and iso-butane.

Maximum amount of olefines is formed at $650 \text{ }^\circ\text{C}$ and it is 53,5 mas.%, gas conversion is 83,8 mas.%, aromatic compounds begin to emanate at $700 \text{ }^\circ\text{C}$ and

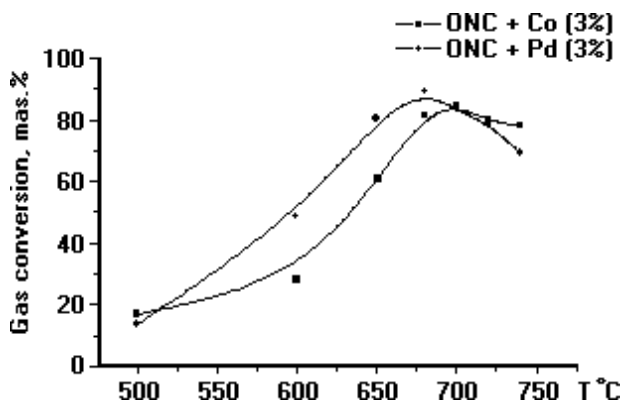


Fig.5 Gas conversion dependence on temperature. ONC + Co (3%) - Overcarbonized Narynkol clay, promoted by cobalt (3%). ONC + Pd (3%) - Overcarbonized Narynkol clay, promoted by palladium (3%).

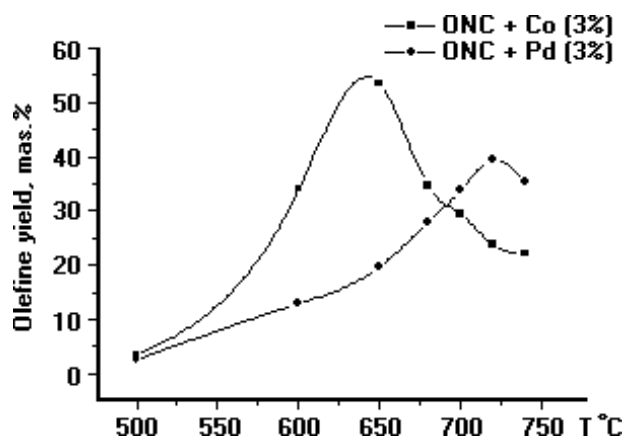


Fig.6. Olefine yield dependence on temperature. ONC + Co (3%) - Overcarbonized Narynkol clay, promoted by cobalt (3%). ONC + Pd (3%) - Overcarbonized Narynkol clay, promoted by palladium (3%).

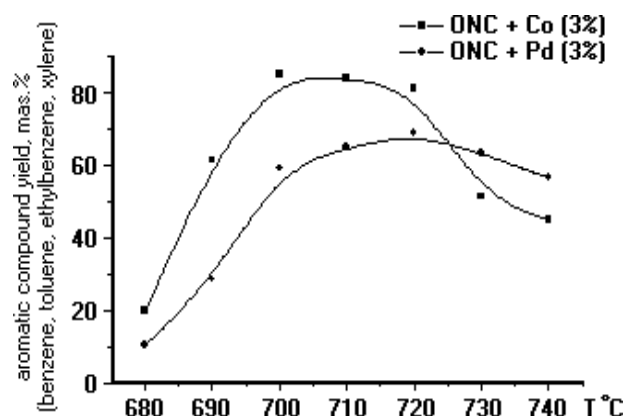


Fig.7. Aromatic compound yield dependence on temperature. ONC + Co (3%) - Overcarbonized Narynkol clay, promoted by cobalt (3%). ONC + Pd (3%) - Overcarbonized Narynkol clay, promoted by palladium (3%).

Table 1

Products of C₃-C₄ hydrocarbon conversion on cobalt - carbon catalyst.

Products	500°C mas. %	600°C mas. %	650°C mas. %	680°C mas. %	700°C mas. %	720°C mas. %	740°C mas. %
H ₂	0,21	0,65	1,32	0,82	1,35	1,57	1,77
CH ₄	1,03	6,5	15,3	13,9	19,5	24,4	21,9
C ₂ H ₆	1,34	16,1	15,7	12,4	12	18,5	25,0
C ₂ H ₄	2,26	18,1	31,9	23	24,6	21,5	18,8
C ₃ H ₈	35,5	22,8	10,8	3,52	2,2	1,72	0
C ₃ H ₆	0,90	12,4	17,8	9,54	3,29	1,83	1,53
iso-C ₄ H ₁₀	9,12	3,37	1,85	0,59	0,19	0	0
C ₄ H ₁₀	34,1	29,4	10,9	2,17	0,72	0,15	0,07
iso-C ₄ H ₈	0,37	4,15	5,57	2,24	1,56	0,48	1,82
C ₆ H ₆	-	-	7,18	11,7	18,7	19	21
Gas conversion, %	16,9	28,3	60,7	81,3	84,8	79,6	78
Σ olefins	3,53	34,1	53,5	34,7	29,4	23,8	22,1
Composition of liquid phase							
C ₆ H ₆	-	-	-	-	37,9	57,7	25,5
CH ₃ C ₆ H ₆	-	-	-	-	37,8	16,9	12
(CH ₃) ₂ C ₆ H ₆	-	-	-	-	4,05	2,57	1,24
C ₂ H ₅ -C ₆ H ₅	-	-	-	-	5,03	3,86	6,21
C ₉₊	-	-	-	-	15,2	18,9	55
Σ aromatics	-	-	-	-	84,7	81	44,9

Table 2
Products of C₃-C₄ hydrocarbon conversion on palladium - carbon catalyst

Products	500°C mas. %	600°C mas. %	650°C mas. %	680°C mas. %	700°C mas. %	720°C mas. %	740°C mas. %
H ₂	0,23	0,49	0,57	0,39	1,3	1,1	1,34
CH ₄	0,74	3,44	5,31	5,9	20,4	24,9	26,6
C ₂ H ₆	16,1	9,89	8,52	5,1	12,6	18,5	28,4
C ₂ H ₄	1,16	10,4	10,9	19	24,8	34,8	31
C ₃ H ₈	34,8	13,3	3,62	1,81	2,73	1,9	1,5
C ₃ H ₆	0,51	4,2	6,29	7,21	2,9	4,05	3,6
iso-C ₄ H ₁₀	7,93	7,22	1,15	0,43	0,04	0	0
C ₄ H ₁₀	27,5	21,1	6,17	3,63	1,25	1,09	0,9
iso-C ₄ H ₈	0,95	4,4	2,65	2,36	1,9	0,73	0,72
C ₆ H ₆	-	-	0,21	3,65	13,8	10,2	15,1
Gas conversion, %	13,6	48,4	80,5	89	83,3	78,5	69,2
Σ olefins	2,62	19	19,8	28	29,5	39,5	35,3
Composition of liquid phase							
C ₆ H ₆	-	-	-	-	23	25,9	14,5
CH ₃ C ₆ H ₅	-	-	-	-	18,9	20,8	17,4
(CH ₃) ₂ C ₆ H ₄	-	-	-	-	3,67	2,45	1,2
C ₂ H ₅ - C ₆ H ₅	-	-	-	-	3,66	4,91	6
C ₉₊	-	-	-	-	50,8	45,9	60
Σ aromatics	-	-	-	-	49,2	54	39,1

correspond to 84.7 mas.%. C₃-C₄ gas conversion in the presence of overcarbonized catalyst, promoted by palladium, is the most effective. Presence of overcarbonized palladium catalyst at 680 °C results in 89 mas.% of gas conversion degree. On promoted by cobalt overcarbonized catalyst at 700 °C gas conversion increases to 84,8 mas.%.

It can be seen from Fig. 5 that in temperature interval of 500-740 °C an increase of gas conversion degree by 5-6 % for overcarbonized palladium catalyst compared with overcarbonized cobalt catalyst is observed.

In contradiction to overcarbonized palladium catalyst maximum olefine yield in the presence of overcarbonized cobalt catalyst at 650 °C is 53,5 mas.%. In the presence of overcarbonized palladium catalyst at 720 °C olefine yield is 39,5 mas.%.

In the presence of overcarbonized cobalt catalyst

aromatic compound yield at 700 °C is 84,7 mas.%. With an increase of temperature from 700 °C to 740 °C aromatic compound yield decreases to 44,9 mas.%. With using of overcarbonized palladium catalyst at 720 °C an increase of aromatic compound yield is observed.

Table 2 shows the results of chromatographic analysis of products of propane-butane mixture conversion in the presence of carbomineral palladium catalyst.

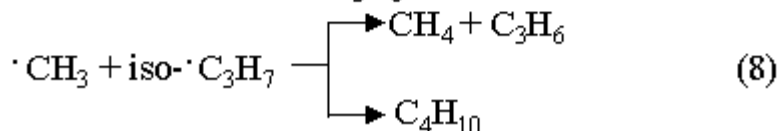
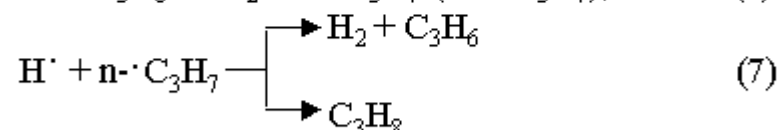
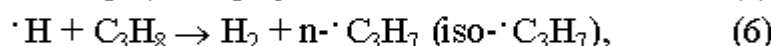
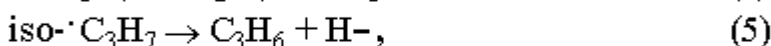
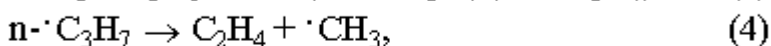
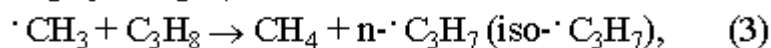
It can be seen from the table that in the presence of palladium-carbonic catalyst in process of C₃-C₄ hydrocarbon conversion great amount of chemical compounds is formed.

Compared results of made studies of process of C₃-C₄ hydrocarbon conversion on carbonaceous palladium and cobalt catalysts show that carbonaceous cobalt catalysts are much more effective in reactions

of olefine and aromatic compound formation.

Formation of observed products of C₃-C₄ hydro-

carbon conversion on palladium-, cobalt- and nickel-carbon catalysts is possible in the following reactions:



Formation of ethylene and propylene, iso-butylene according to above-cited scheme occurs in result of hydrocarbonic radical decomposition and their interaction with the atom of hydrogen.

After studies made on using of overcarbonized cobalt and palladium catalysts on the base of mineral raw-materials of Kazakhstan in process of C₃-C₄ hydrocarbon cracking it is shown that above mentioned catalysts are effective and cheap. Efficiency of metal-carbonic catalysts can be explained by formation of active centers in form of particles of reduced metal on the surface of catalyst.[9]

Conclusion

Thus, as a result of made studies on carbonaceous cobalt and palladium catalysts formation of 53,5 mas.% of olefines, 84,7 mas.% of aromatic compounds is obtained, and it is shown, that metal (cobalt) is an active center of catalyst.

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