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APPLICATION OF ZEOLITE CATALYSTS IN CONVERSION PROCESS OF HYDROCARBONS C_2-C_4

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Nowadays there are utilization problem of huge gaseous hydrocarbon discharge amount on natural gas and petroleum production sites. Considerable part of hydrocarbon stock was simply burned in flares on oil production regions for lack of acceptable refinement processes. It is very important to solve this problem for ecological and energy saving needs of our country. Conversion process of associated petroleum gas to aromatic hydrocarbons, blending fuels is perspective option in resolution of the problem. One of these processes is catalytic hydrocarbon conversion on zeolite catalysts. Zeolites are widely applied in a majority of catalytic processes of petroleum refinery. There are many uses of these catalysts in such reactions as hydrodewaxing, fluid catalytic cracking, gasoline desulfurization, etc. All these application are available because of shape selective properties of zeolites, e.g. ZSM-5.

The purpose of given work is examination of zeolite catalyst effect on hydrocarbon conversion process.

In our research we used MFI-type zeolites synthesized on organic framework structures or templates by crystallization. There are two types of zeolites: H-ZCE-H (Hexamethylenediamin as template) and H-ZCE-AF (mixture of cyclohexanone and cyclohexanol as template). At first zeolite powder was pressed in tablet under pressure of 200 kgf/cm^3. Then the tablet was pressed through the sieve with cell diameter of 2mm and weighed. Several industry-used zeolite catalysts were also examined (e. g. Sud-Chemie and KN-30). We carried out experiment on vertical flow reactor with stationary catalyst phase. Cubic capacity of catalyst used was 6 cm^3. Temperature range was 525- 600 °C, WHSV = 240 h^{-1}, P = 1 ATM. Initial stock composition was: methane – 0,2%, ethane – 2,8%, propane – 81,1%, butane – 12,1%. Quality and quantity analysis was performed by gas chromatography method with using gas chromatograph “Chromatek-Crystall 5000M”. Separation of gaseous products was carried on packed column (l=3m, d= 3mm) filled with 8% NaOH/ Al_2O_3 on thermal conductivity detector. Liquid products were detected on flame ionization detector, separation took place on DB-1 capillary column l = 100m, d = 0,25mm, film thickness = 0,5mkm, gas carrier - helium.

The results of zeolite catalysts examination are presented in the Table.

Table

Process temperature effect on product composition of associated petroleum gas conversion on different ZSM-5-type (MFI) catalysts, WHSV= 240 h^{-1}

Catalyst	Sud-Chemie			KN-30			H-ZCE-H			H-ZCE-AF		
Temperature, °C	550	575	600	550	575	600	550	575	600	550	575	600
∑ Conversion, %	69,5	80,2	87,9	61,2	72,3	81,2	90,8	95,0	96,9	86,9	90,4	92,5
Methane	23,7	30,2	37,0	17,6	25,2	32,9	42,6	45,9	48,1	39,9	41,1	41,0
Ethane	11,4	11,8	11,8	9,1	10,3	10,9	17,9	16,5	15,4	17,8	15,9	14,1
Ethylene	7,3	9,6	11,9	7,5	10,2	13,0	4,7	5,9	7,1	5,3	7,3	9,8
Propane	36,8	25,2	15,9	48,7	37,5	27,0	13,0	7,5	4,7	18,1	13,7	11,1
Propylene	7,8	8,7	9,0	7,9	9,2	10,0	3,8	3,8	3,8	4,5	5,4	6,3
Isobutane	1,4	0,72	0,33	2,3	1,5	0,8	0,35	0,16	0,08	0,54	0,34	0,23
Butane	1,0	0,53	0,24	1,3	0,8	0,4	0,31	0,15	0,07	0,43	0,25	0,14
Benzene	5,6	8,0	11,1	4,5	7,4	10,5	12,2	15,9	18,2	13,5	14,5	16,4
Toluene	28,5	33,0	36,3	27,6	32,2	36,0	33,7	34,9	34,7	36,9	37,6	39,8
m-Xylene	16,8	15,0	12,9	17,6	15,5	14,0	10,5	9,1	8,5	11,3	10,8	10,5
p-Xylene	6,7	6,3	5,6	7,4	6,6	6,0	4,5	4,0	3,8	5,1	4,8	4,7
o-Xylene	8,1	7,4	6,5	8,8	7,8	7,0	5,0	4,4	4,2	5,3	5,1	5,0
Naphthalene	1,7	2,0	2,9	2,5	2,9	3,1	6,9	7,1	7,4	8,5	7,8	7,7
β-methylnaphthalene	3,1	3,3	3,5	3,9	3,6	3,4	7,1	6,6	6,4	5,4	4,7	4,2
α-methylnaphthalene	1,5	1,6	1,7	1,9	1,7	1,6	3,3	3,2	3,1	2,1	1,9	1,7

As we can see from previous data, conversion level is rising with elevation of temperature for all samples. This is mostly because of increasing yield of light alkanes (methane, ethane) and arenes with one aromatic ring (benzene, toluene). Conversion level is higher for H-ZCE-H and H-ZCE-AF samples than for industrial ones. This is basically on account of higher yield of methane and naphthalene fraction. At the temperature higher than 600°C conversion level is going down and yield of almost all products is dropping except light alkanes (methane, ethane) and benzene. It can be accounted for increasing extent of cracking.

In gaseous products we can observe content rise of methane and decrease of propane, butane and isobutane for all samples with temperature growth because of cracking process. There are also increasing amount of olefins (ethylene, propylene) due to dehydrogenation process. It should be noted that industrial catalysts have higher selectivity on olefins and propane than laboratory ones. H-ZCE-H and H-ZCE-AF, in their turn, have higher selectivity on methane and ethane. As for the liquid products, there are increasing of benzene and toluene and decreasing of xylenes with temperature growth for all samples. Naphthalene content rises with temperature for Sud-Chemie, KN-30 and H-ZCE-H samples but drops for H-ZCE-AF zeolite. It can be explained by increasing cracking process of substituted naphthalenes to naphthalene and olefins in case of Sud-Chemie, KN-30 and H-ZCE-H. On H-ZCE-AF zeolite the process probably is going further to decyclization because of its larger cavities. In order to prove it we can cite for large amount of toluene in product mixture in comparison with other catalysts, because toluene is one of naphthalene decyclization products. Sud-Chemie and KN-30 catalysts have higher selectivity on xylenes but lower one on benzene, toluene and naphthalenes.

Therefore, the research of zeolite catalysts indicated that laboratory synthesized zeolites have higher conversion level in comparison with industrial ones. They also have higher selectivity with aromatics such as benzene, toluene and naphtalenes. Moreover, the yield of aromatics can be improved by adding special additives e.g. metal oxides, heteropolicompounds and so on. Thus, the zeolites are very promising catalysts in obtaining a wide range of aromatic compounds due to their high activity and selectivity.

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FORECASTING OF PERSPECTIVE OIL-BEARING AREAS BASED ON MAGNETIC ANOMALY TRANSFORMATIONS

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The application of magnetic survey has traditionally been limited to the exploration of regional peculiarities of geological structures, composition of crystalline plate basement. Due to weak magnetic characteristics of sedimentary rocks the sedimentary mantle has commonly been excluded from the survey targets. Implementation of modern, high accuracy equipment made it possible to reveal high-frequency anomalies associated with the deposits of hydrocarbons [1].

At present a set of high accuracy magnetic surveys were conducted over several fields in the south-eastern part of Western Siberian Plate. The research workers of Tomsk Polytechnic University (Merkulov V.P., Zyatev G.G. 2000, 2003) conducted the analysis of the obtained findings, whose results are shown in Figure 1.

Over the Archinskoe gas condensate field there occur “micromagnetic anomalies” which represent the zones of great contrast in magnitude of high-frequency magnetic field superimposed upon low-frequency anomaly background. Regional anomalies connected with deep-lying structure are eliminated through averaging, while high-frequency anomalies contain data about plate sedimentary mantle and zones of its epigenetic transformations including the top part of the section.

High-frequency areas distinguish the so-called “magnetic covers” associated with hydrocarbon deposits and zones of epigenetic transformations (according to Merkulov V.P.).

Frequency analysis applied by V.P. Merkulov was supplemented by investigations of spectral sections. In these procedures the frequency spectrum was estimated with running window (51 points), and the spectrum sections were produced considering that depths of anomaly causing structure are determined as half periods of the estimated spectrum. The technique was tested in the Achinskoe, Krapivinskoe, Yuzhno- Cheremshanskoe, Gerasimovskoe fields, whose hydrocarbon depositions are confirmed to different stratigraphical intervals varying from the Paleozoic to the Cretaceous formations [2]. Reliability of forecasting constitutes 84% and it is proved by data obtained through drilling exploratory and production wells in the Krapivinskoe and Yuzhno-Cheremshanskoe fields. However, it is impossible to say with high degree of certainty that the discovered regularity will be observed in any type of a deposit. Consequently, the objective of the conducted research is to evaluate the effectiveness of the mentioned technique in the Selimkhanovskoe oilfield.

The magnetic surveys over the site were carried out in 2008, but the described technique was not applied for forecasting deposits. With respect to administrative division the survey area is located within Parabel region of Tomsk oblast. Considering tectonics the site is a part of the Pudinsky elevation comprising several faults. The geological section can be divided into two layers. The bottom layer is Pre-Jurassic basement and the top layer contains Mesozoic and Cainozoic plate mantle. Oil is restricted to the Tyumen, Naunac and Georgiev suites.