RJC

RASĀYAN *J. Chem.*
Vol. 13 | No. 3 |1444-1450| July - September | 2020
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

CATALYTIC CRACKING USING CATALYSTS BASED ON HETERO POLYACIDS

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ABSTRACT

The paper discusses the issues of catalytic cracking processes and presents the experimental results of the authors with the use of the catalysts based on the natural Shankanai zeolite (Kazakhstan) and heteropoly acids (HPA). SEM analysis of the synthesized catalyst structure indicates the presence of its main elements prevailing on the surface of the zeolite. Also, the intense spectra of the components of the HPA (tungsten and phosphorus) are revealed. Possibly, it is because of the high degrees of dispersion and distribution of PW_{12}-HPA particles over the clinoptilolite surface. In this research an analysis of the final reaction product was carried out by NMR spectroscopy. NMR analysis allowed us to calculate the fraction of each component of the mixture. It was shown that the proton spectrum of the sample contains signals of paraffin compounds, which are the main components of the mixture. Aromatic components are absent. Chemical shifts of up to 1 ppm are characteristic mainly of protons of the methyl groups of saturated hydrocarbons and long alkyl substituents in aromatic systems. In this part of the spectrum, it is also assumed that some CH and CH_2 groups of naphthenic fragments are resonated.

Keywords: catalytic cracking, heteropoly compounds, NMR spectroscopy, petroleum products, oil products analysis.

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INTRODUCTION

Modern automobile gasoline is one of the most qualified and expensive energy carriers. For their production, a complex set of technological processes for purification and conversion oil processing as well as various additives that ensure compliance with modern requirements for the composition and quality of this type of motor fuel are used.[1-4] More than 600 refineries operate in the world to provide fuel for the car fleet, with a total capacity of almost 4.5 billion tons of oil per year, and more than 2 billion tons of gasoline is produced. Catalytic cracking is the most dynamically developing process of oil refining. In its development, the process of catalytic cracking has gone through several stages.[5-13] The most important event in the improvement of the catalytic cracking process was the use of zeolite-containing catalysts.[13-16] The activity of catalytic cracking catalysts over the past almost 80 years has increased more than 300 times. The main advantage of the catalytic cracking is greater operational flexibility: the ability to process various oil fractions.[15-25] The target product is a high-octane component of gasoline with an octane number of 90 points or more, its yield is from 50 to 65% depending on the raw material used, the technology used and the mode. The high octane number is because isomerization also occurs during catalytic cracking.[25-27] Currently, the main raw material for catalytic cracking is vacuum gas oil, a straight-run fraction with boiling limits of 350-500°C. The end of boiling is determined mainly by the content of metals and the coking ability of the raw material, which should not exceed 0.3%.[26-34] Catalytic cracking gasoline contains mainly saturated hydrocarbons, most of which are branched-chain hydrocarbons. Therefore, catalytic cracking gasoline has a greater detonation resistance (due to the presence of branched hydrocarbons) and greater oxidation stability (due to a lower content of unsaturated

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hydrocarbons) and it is a more valuable fuel.[33-35] Table-1 shows the dependence of the yield of gasoline and coke on various types of hydrocarbon feedstocks.

Table-1: Gasoline Yield Depending on the Type of Hydrocarbon Feed

Conversion, % vol.	Hydrocarbon Raw Material		
	Paraffinic	Naphthenic	Aromatic
60.0	58.65	55.15	50.70
65.0	62.14	58.27	53.16
70.0	64.82	60.63	54.21
75.0	66.89	61.96	51.93
80.0	67.64	60.86	50.05
85.0	66.13	56.73	40.12

In the process of catalytic cracking, the following products are formed: dry gas, propane-propylene and butane-butylene fractions, stable gasoline, light gas oil and bottoms product (heavy gas oil).[33-35] The yield and quality indicators of gaseous products were not determined since the target product of catalytic cracking is gasoline (stable). Yields and quality parameters of the products obtained are given in Table-2.

Table-2: Yields and Quality Indicators of Stable Gasoline

Quality indicators	Parameter values
Yield on raw materials, % by wt.	48.8-53.0
Relative density at 20°C	0.743-0.744
Fractional composition, °C	
Beginning of boiling	45-47
10%	56-59
50%	102-104
90%	110-185
The end of boiling, maximum	202
The content of sulfur, ppm	no more than 131
Octane rating	
Research method	90.5-91.5
Motor method	80.3-80.8

EXPERIMENTAL

Analysis of the Obtained Product Using NMR

In this research an analysis of the final reaction product was carried out by NMR spectroscopy. As a method of quantitative analysis, modern high-resolution NMR spectroscopy began to be widely used in the control of the quality of oil and oil products.[36,37] NMR spectroscopy is a modern spectroscopic method for the study of chemical compounds. Information on complex organic systems by NMR can be obtained in the form of isotopic, elemental, fragment and component composition. NMR spectroscopy takes into account data on the position, intensity and multiplicity of signals in the spectrum (component composition), the integrated intensities of specific regions of the spectrum (fragment or structural-group analysis).[36,37] Quantitative determination of the ratios of components in a mixture can be done by calculating the integral intensities of an atom or groups of atoms characteristic of one or another component. In this work, the spectra of the sample were registered on the JNN-ECA 400 spectrometer of the company "Jeol" (Japan). The operating frequency of the spectrometer is 400 and 100 MHz on ^{1}H and ^{13}C cores, respectively. The survey was performed at room temperature using $CDCl_3$ solvent. Chemical shifts are measured relative to the signals of residual protons or carbon atoms of deuterated chloroform.

Catalysts Synthesized on the Base of Heteropolyacids (HPA)

Heteropoly acids are complex acids whose anion is formed by two different acid-forming oxides. A molecule of one of them accounts for several molecules of the other.[38] According to Vernadsky, heteropoly acids also include aluminosilicate acids, whose salts he considered aluminosilicates. Heteropoly acids (HPA) are proton compounds with the complex anion of inorganic polyoxometallates (molybdenum, tungsten or vanadium).[39-41] Heteropoly acids of the 12th series with the so-called "Keggin

heteropolyanion" are of the greatest importance for catalytic processes. In the present study, catalysts based on the natural zeolite of the Shankanai deposit modified with mineral, organic acids and HPA, were prepared for catalytic cracking. The method of preparation of catalysts is described in our previous works.[42]

RESULTS AND DISCUSSION

Analysis of the Synthesized Catalyst on the Base of Natural Zeolite and HPA

Previously we have found that as a result of modification of the HPA zeolite, HPA is temporarily bound to the zeolite.[42] According to SEM, high degrees of dispersion and distribution of PW_{12}-HPA particles on the clinoptilolite surface were detected. In the thin layers of the PW_{12}-HPA/H-Z-1 catalyst (where Z is a zeolite), darkenings of various shapes and contrasts are visible. The results of the study on the EDAX spectrometer confirm that such darkenings have the same compositions with PW_{12}-HPA. It should be noted that the dispersion of PW_{12}-HPA particles on the clinoptilolite surface is high compared to the sizes of PMo_{12}-HPA (1-10 μm), while the modified HZ layered structures are coated with PMo_{12}-HPA agglomerates uniformly distributed and strongly bonded to the clinoptilolite surface (Fig.-1 and 2).

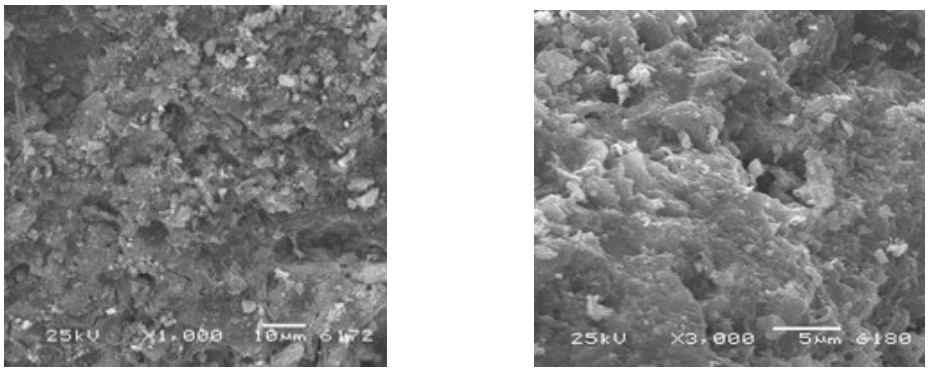

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Fig.-1:SEM images of the PW_{12}-HPA / HZ catalyst, resolution 1cm = 50 and 1 μm.

On the surface of the zeolite the content of its main elements prevail, at the same time, the intensities of the spectra of the components of the heteropoly acid (tungsten and phosphorus) are manifested. This is due to the high degrees of dispersion and distribution of PW_{12}-HPA particles over the clinoptilolite surface.[38-40]

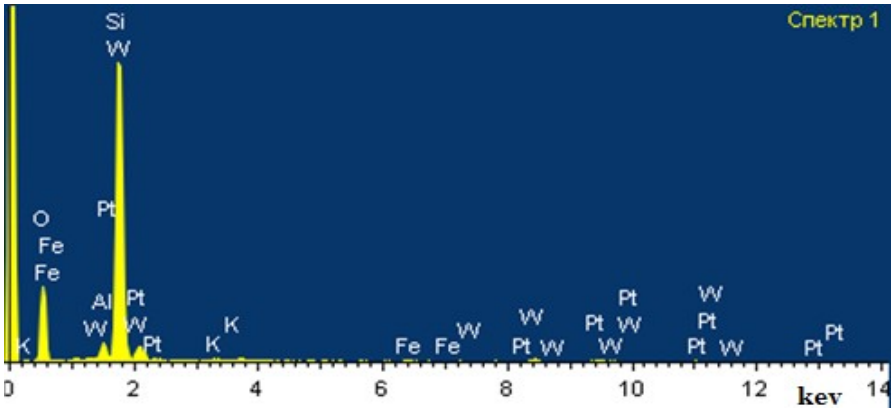


Fig.-2: Elemental analysis of the scanned portion of the catalyst PW_{12}-HPA/NZ

Analysis of NMR Spectra of the Product Obtained by Catalytic Cracking Using HPA-Based Catalyst

It was found that the proton spectrum of the sample contains signals of paraffinic compounds, which are the main components of the mixture. Aromatic components are absent. The range of aliphatic hydrogen atoms (0.5-4.5 ppm) is usually divided into three main areas (Table-3). Chemical shifts up to 1 ppm predominantly characteristic of protons of methyl groups of saturated hydrocarbons and long alkyl substituents in aromatic systems.[36]

Also, in this part of the spectrum, it is assumed that some CH and CH_2 groups of naphthenic fragments are resonated.[36,37,43] High-intensity signals at 0.91 and 1.30 ppm indicate a large number of methylene groups of paraffin chains. Range from 1 to 2 ppm also characterized by resonance lines of β-methyl and methylene groups concerning the aromatic nucleus.[37]In the region of 2.0-2.25 ppm. resonance of protons of CH groups of saturated cyclic and acyclic fragments is characteristic. Aromatic methyl substituents give signals at a frequency of 2.43 ppm. The signals of protons of the CH_2 and CH groups at the α-positions to aromatic systems (2.7-4.5 ppm) and protons of olefin fragments (4.5-6.0 ppm) were not noted. The signals from the terminal methyl groups of long alkyl chains (14.10 ppm) were found in the carbon spectrum of the test sample. Methylene and methine groups of alkyl substituents resonate at a frequency of 25.34-44.57 ppm. The presence of olefin (δ = 108-118 ppm) and tertiary carbon atoms in the O and N heteronuclei (δ = 105-120 ppm) has not been established. The scale of the chemical shift of the proton and carbon spectra can be divided into several most important ranges (Tables-3, 4).
Having integrated these spectral regions on ^1H and ^{13}C nuclei (Figures-3, 4), we can calculate the fraction of each component of the mixture using the following equations:

$H_{general} = H_{ar} + H_{ol} + H_\alpha + H_\beta + H_\gamma$ (total integrated signal strength ^1H)
$H_{ar} = H_{ar}/H_{general} \cdot 100\%$ (the percentage of aromatic protons)
$H_{al} = (H_\alpha + H_\beta + H_\gamma)/ H_{general} \cdot 100\%$ (the percentage of aliphatic protons)
$H_\alpha = H_\alpha/H_{general} \cdot 100\%$
$H_\beta = H_\beta/H_{general} \cdot 100\%$
$H_\gamma = H_\gamma/H_{general} \cdot 100\%$ (the percentage of protons in α-, β- and γ positions, respectively)
$n_H = (H_\alpha + H_\beta + H\gamma)/H_\alpha$ (carbon chain length according to ^1H NMR spectrum)
$C_{ar} = C_{ar}/(C_{ar}+C_{al}) \cdot 100\%$ (the percentage of aromatic carbons).
$C_{al} = C_{al}/(C_{ar}+C_{al}) \cdot 100\%$ (percentage of aliphatic carbon atoms).[37]

Table-3: Ranges of Chemical Shifts ^1H of Petroleum Products[37]

δ (^1H), ppm	Atom Designation	Functional Group
0.5-1.0	H_γ	CH_3 groups of saturated compounds. CH_3 groups in the γ-position and further positions to the aromatic ring.
1.0-2.0	H_β	CH_2 and CH groups of saturated compounds. Protons of β-methyl, β- and further positions of methylene and methine groups at the aromatic ring.
2.0-4.0	H_α	Protons of groups in the α-position to aromatic and carbonyl carbons, heteroatoms.
4.5-6.0	H_{ol}	Olefin groups
6.0-9.0	H_{ar}	Hydrogen atoms of aromatic nuclei, phenolic hydroxyls

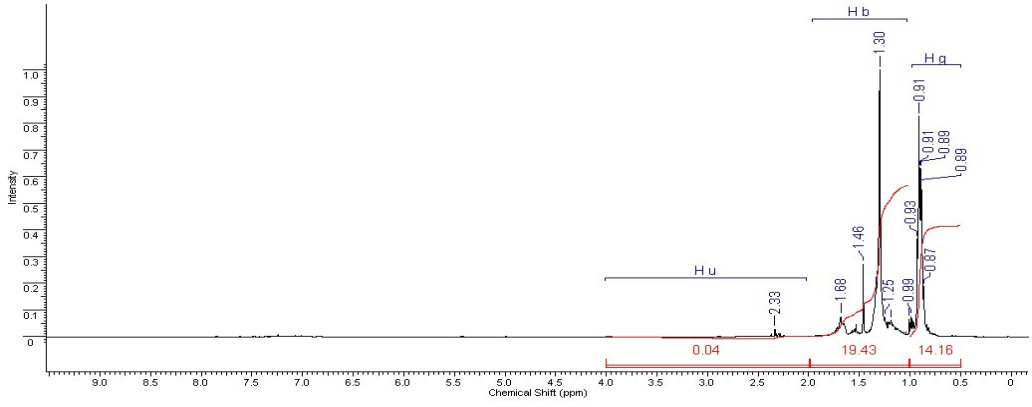
Table-4:The Ranges of Chemical Shifts ^{13}C of Petroleum Products[36,37]

δ (^{13}C), ppm	Atom Designation	Functional Group
7-17	$C_{p.n}$	Primary carbon atoms in the methylene group.
17-25	C_{pa}	Primary carbon atoms bonded to CH group or aromatic nucleus.
17-50	C_{s+q}	Secondary and quaternary C atoms of saturated compounds
25-65	C_{al}	Aliphatic CH groups.
25-50	C_q	Quaternary carbon atoms of saturated compounds.
108-118	C_{ol}	Olefin fragments.
110-135	C_{at}	Tertiary C atoms of aromatic systems.
130-137	C_{msca}	Methyl-substituted aromatic carbon atoms.
137-148	C_{alk}	Alkyl and naphthyl substituted carbon atoms of aromatic nuclei.
148-170	C_{arp}	Aromatic carbon atoms substituted with a phenolic or ether group
170-200	C_c	Carbonyl carbon atoms

The calculation results are presented in Table-5.

Table-5: Fragment Composition of the Sample

No	Atom Type	Quantity (%)
1	H_{ar}	0
2	H_{ol}	0
3	H_{al}	100
4	H_{α}	0.11
5	H_{β}	57.78
6	H_{γ}	42.11



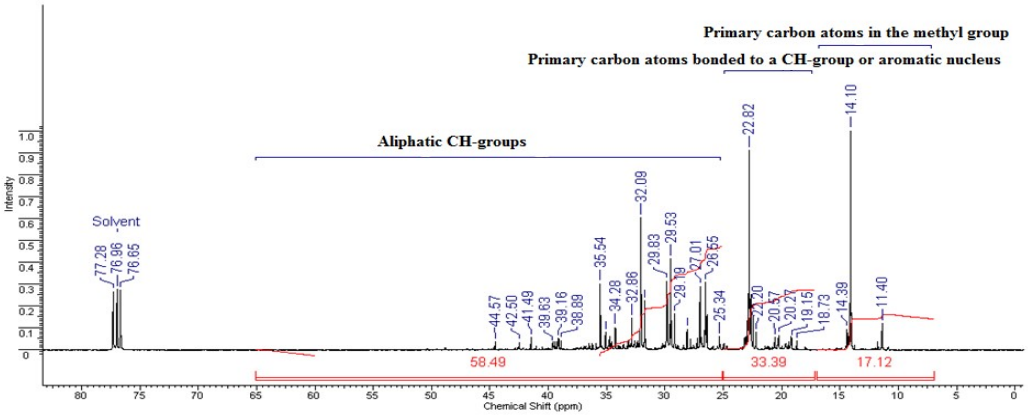
No.	(ppm)	(Hz)	Height
1	0.87	346.1	0.1887
2	0.89	355.2	0.5616
3	0.89	357.7	0.6288
4	0.91	361.9	0.6308
5	0.91	365.0	0.8261

No.	(ppm)	(Hz)	Height
6	0.93	371.7	0.3651
7	0.99	394.9	0.0754
8	1.00	401.6	0.0656
9	1.19	474.9	0.0610
10	1.25	498.7	0.0718

No.	(ppm)	(Hz)	Height
11	1.30	518.8	1.0000
12	1.34	534.1	0.1843
13	1.46	583.5	0.2715
14	1.68	673.2	0.0748
15	2.33	932.6	0.0272

No.	(ppm)	Value	Absolute Value
1	[2.00 .. 4.00]	0.035	2.97361e-1
2	[0.50 .. 1.00]	14.163	1.19477e+2
3	[1.01 .. 1.99]	19.427	1.63882e+2

Fig.-3:[1]H Spectrum of Catalytic Cracking Product



No.	(ppm)	(Hz)	Height
1	11.40	1146.5	0.1190
2	14.10	1417.7	1.0000
3	14.39	1446.5	0.0925
4	18.73	1882.6	0.0370
5	19.15	1924.7	0.0499
6	20.27	2037.8	0.0626
7	20.57	2067.5	0.0541
8	22.20	2231.4	0.0781
9	22.82	2293.7	0.9099
10	25.34	2547.7	0.0572
11	26.55	2668.5	0.3058

No.	(ppm)	(Hz)	Height
12	27.01	2715.5	0.2881
13	28.10	2824.7	0.0918
14	29.19	2934.0	0.1624
15	29.53	2968.5	0.4141
16	29.83	2998.2	0.3118
17	31.74	3190.9	0.2208
18	32.09	3225.4	0.6026
19	32.86	3303.0	0.1431
20	34.28	3445.8	0.1006
21	35.11	3529.2	0.0781
22	35.54	3572.3	0.3002

No.	(ppm)	(Hz)	Height
23	38.89	3909.7	0.0384
24	39.16	3936.6	0.0493
25	39.63	3983.5	0.0253
26	41.49	4170.4	0.0547
27	42.50	4272.0	0.0320
28	44.57	4480.0	0.0331
29	76.65	7705.2	0.2704
30	76.96	7736.9	0.2742
31	77.28	7768.5	0.2632

No.	(ppm)	Value	Absolute Value
1	[6.96 .. 16.97]	17.122	5.48449e+0
2	[17.14 .. 24.97]	33.388	1.06949e+1
3	[25.06 .. 65.05]	58.488	1.87349e+1

Fig.-4:[1]H Spectrum of Catalytic Cracking Product

CONCLUSION

The paper describes catalytic cracking development as well as the experimental results of the authors. The analysis data show that on the surface of the zeolite the content of its main elements prevails, but the

intensities of the spectra of the components of the heteropoly acid (tungsten and phosphorus) are revealed. Data of NMR-spectroscopy shows that the proton spectrum of the sample contains signals of paraffinic compounds, which are the main components of the mixture. Aromatic components are absent. The range of aliphatic hydrogen atoms (0.5-4.5 ppm) is usually divided into three main areas. Chemical shifts up to 1 ppm predominantly characteristic of protons of methyl groups of saturated hydrocarbons and long alkyl substituents in aromatic systems. Range from 1 to 2 ppm also characterized by resonance lines of β-methyl and methylene groups concerning the aromatic nucleus. In the region of 2.0-2.25 ppm resonance of protons of CH groups of saturated cyclic and acyclic fragments is characteristic. Aromatic methyl substituents give signals at a frequency of 2.43 ppm.

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[RJC-5822/2020]