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ZEOLITE CONTAINING (HY+HZSM-5) CATALYST ON PILLARED Al-MONTMORILLONITE FOR CRACKING OF WEIGHTED VACUUM GAS OIL

Abstract. Data on efficiency of bizeolite HY + HZSM aluminum pillared catalysts on montmorillonite in the cracking of weighted vacuum gas oil and correlations of catalysts activities with their physico-chemical characteristics are given. The content of each zeolite was 15%. The weight ratio of zeolite HY and HZSM is 1:1. Used HY and HZSM-5 zeolites had silica modulus equal to 38 and 51 respectively. The carrier of zeolite catalyst was Al-pillared Tagan montmorillonite in Na-form without preliminary acid activation. Concentration of pillared agent - oligomeric aluminum hydroxocomplex was 2.5 and 5.0 mmol Al^{3+}/g NaMM. The catalyst was prepared by mechanical mixing of matrix and zeolite. The cracking was carried out in standard laboratory apparatus with 40 ml of catalyst in the temperatures range 500-550^{0}C. To determine the structural characteristics of catalysts there were used methods: BET, XRD, temperature programmed desorption (TPD) of ammonia, temperature programmed reduction (TPR) catalyst with hydrogen. Gasoline and cracking gases were analyzed by gas-chromatogram.

It is shown that the quantity of gasoline (17%) and light gas oil (37%) formed on HY - sample exceeds data on HZSM-contact (9 of 30%, respectively). The amount of gaseous products formed over the HZSM - 5 catalyst is more than 2 times higher than the quantities of gases on the HY - containing catalyst.

On the base of the ammonia TPD data it was concluded that the increased gas production on HZSM - catalyst is responsible for big compared to HY - zeolite total acidity of the contact (274 and 250 umol NH_3/g, respectively) and a large quantity(28%) of strong acid sites. We found that Al (5.0)NaMM + HZSM-5 zeolite catalyst is responsible for the strong aromatization of hydrocarbons.

HY + HZSM bizeolites catalyst on Al (2.5) NaMM support has high specific surface area and a large number of micropores (67.1%) defined by narrow porous zeolite HZSM -5 compared with HY -zeolite. Increasing of cracking temperature to 600^{0}C results in a 35.6% yield of the gas phase to the feed raw material. 45% propylene and 17.8% butenes and iso-butene were determined in the gas phase.

Key words: cracking, catalyst, montmorillonite, matrix, pillaring.

Introduction

At present, it produces about 500 tonnes of cracking catalysts for various purposes in the world, which control 95% of market catalysts [1,2]. From the beginning of the 90s the world's leading oil companies are developing a process of deep catalytic cracking, the most cost-effective process for producing light olefins (mainly, propylene and butylene) from various hydrocarbon feed stocks. The distinctive sign of this process is primarily the use of new zeolite containing cracking catalysts. A necessary component of such catalysts is zeolites of ZSM-5 type.

It is generally recognized that pentasils sorption properties depend both on the diameter and shape of the channels. [3-6]. Specificity of the geometry, the high density of the crystalline lattice, a high molar ratio of SiO_2/Al_2O_3, high thermal stability of the frame (~ 1400^0C) are of great interest and determine the extensive use of high-silica zeolites in petrochemical processes [5-9].

The ability of pentasils to easily adsorb and selectively split (selective cracking) of normal paraffins structure make these zeolites perspective cracking catalysts as individual hydrocarbons and highly paraffinic petroleum fractions [9-15]. High thermal resistance of HZSM - 5 zeolites can be used in the process of deep catalytic cracking to produce light olefins [12,13].

The basis of the technology production of zeolites containing catalysts [14-20] consist of a number of principles, have influence on their catalytic properties: a balanced activity of zeolites Y and ZSM-5 in the catalyst structure; the use of semi-synthetic matrix using natural bentonite clay; activity matrix which can be regulate by changing the ratio of protoned and aprotoned acid sites.

The composition of bizeolite catalyst includes two types of zeolites. Zeolite HY, with a faujasite structure with a size of input windows 0.74 nm performs cracking of C_{14}-C_{20} and higher hydrocarbons forming the gasoline range hydrocarbons (C_7-C_8). However, the high rate of hydrogen redistribution reactions on zeolites Y negative influence on the formation of olefins. For secondary cracking of hydrocarbons C_7-C_8 into the catalyst composition zeolite HZSM-5 is introduced. Balanced activity of the zeolite catalyst components, it is possible to increase the yield of C_7-C_8 olefins while maintaining sufficiently high yield of high-octane gasoline [14-20].

For example of the cracking of higher alkanes in [19,20] the role of each component of bizeolite catalyst was shown. It is proved that on the catalysts with an inert matrix, the selectivity of the normal structure of hydrocarbons significantly increases. On a matrix with a relatively high acid properties increases selectivity of low molecular weight C_3 to C_5 alkanes and C_4-C_5 iso-alkanes. The yield of olefins increase in two times, the formation of which is determined by the HZSM-5 zeolite in the catalyst of deep catalytic cracking. Ultrastable zeolite Y is responsible for the selective production of iso-paraffins and aromatic hydrocarbons. In the cracking of real vacuum gas oil, the higher acidity of the matrix is, the higher the yield of C_2-C_4 olefins is.

From the literature data it can be concluded that the direction of the cracking reaction is defined by the catalyst composition and the conditions of the process. Increasing the yield of the gas phase can be achieved by introduction of HZSM-5 - zeolite in the catalyst cracking and increased temperature. The aim of this work was to study the efficiencies bizeolite HY + HZSM-5 catalysts with a weight ratio of zeolites (1: 1) on Al pillared Tagan montmorillonite in catalytic cracking of vacuum gas oil (VG) and the determination of the correlation of activities with the physico-chemical characteristics of catalysts.

Experimental

Al-pillared clays with composition of 5.0 and 2.5 mmol Al^{3+} /g NaMM were prepared. Synthesis of oligomeric aluminum hydroxocomplex $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$($Al_{13}^{7+}$) was carried out as described in [21] by hydrolysis $AlCl_3$ with NaOH aqueous solution until a final pH = 4.5. Pillared material is washed from the Cl - ions. Wet pillared material is mixed with HY and HZSM-5 - zeolite (15 wt%) was formed into pellets, dried overnight at room temperature, then at 150^0 C (2 hours) and 550^0C (2 hours). The catalyst was tested in the cracking VG Pavlodar petrochemical plant (PPCP).

Cracking was carried out in a laboratory flow installation fixed bed at various flow rates. The fraction of gasoline $T_{b.b}$-205^0C and light gas oil (LG) T=205-350^0C. The activity of the catalyst was evaluated by the yield of gasoline and the sum of light products. Gasoline and cracking gases were analyzed by gas-chromatogram. The gas chromatograph was performed on products "Chrom-5" with column (3.5 0,003 m), filled by fluorinated alumina company (USA) «Supelco» (USA). Gasoline samples were analyzed by gas-liquid chromatography by ASTM D 6729-04, on a Kristallux - 4000 M chromatograph with a flame ionization detector (FID), capillary column DB-Petro with an program «NetCrom V2.0». Using helium as the carrier gas.

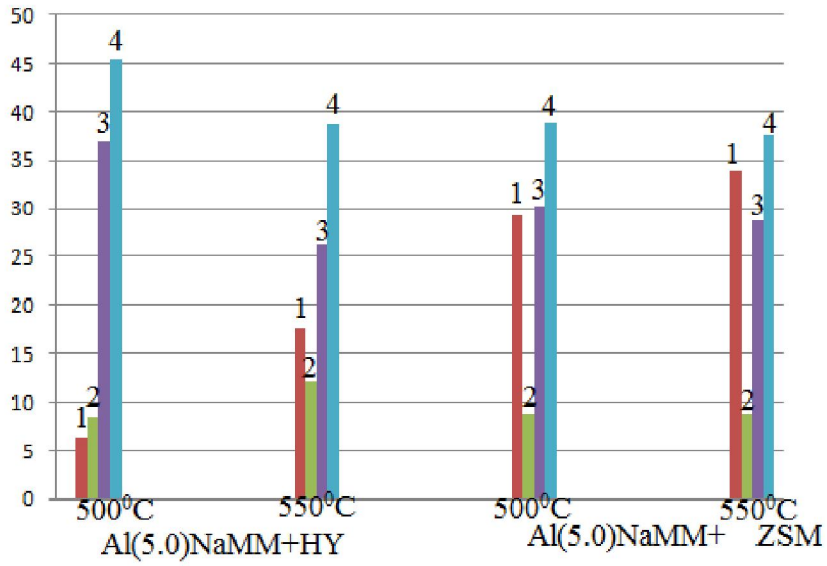
Textural characteristics of catalysts were determined by the nitrogen adsorption isotherms and desorption using apparatus "Accusorb" (BET method). Control of the phase composition was carried out by X-ray on the device DRON-4 * 0.7 with CuKα - radiation. Analysis of the physical and chemical characteristics of zeolite catalysts on Al (5.0) NaMM shows that compared to the original NaMM at

pillarization growing basal reflex (XRD) of 11.9 Å for the NaMM to 14.0 and 14.6 Å, for Al (5.0) NaMM + HY and Al (5.0) NaMM + HZSM-5 catalyst, respectively. The specific surface area increases from 48.2 m^2/g for NaMM to 180.7 and 146.8 m^2/g for HY- and HZSM-containing catalysts. The quantities of mesopores are 76.6, 82.6 and 90.8% for NaMM, Al(5.0)NaMM + HY and Al(5.0)NaMM+HZSM-5, respectively.

Temperature programmed reduction of the catalyst was carried out on high-precision instrument designed to study heterogeneous catalysts Termo Scientific TPDRO 1100 (Aberdeen University. School of Engineering, Scotland). The oxidized catalyst was subjected to software-controlled heating in a stream of 5% hydrogen in nitrogen mixture at temperatures in the range 40-900^{0}C with temperature rise rate 5^{0}C/min.

Results and discussion

From a comparison of performance data of HY and HZSM - zeolite catalysts (Figure 1) follow that the increase of cracking temperature from 500^0 to 550^{0}C both catalysts results in increased gas formation. The amount of gaseous products formed on HZSM-5 zeolite catalyst is more than 2 times their quantity on HY - catalyst. Thus, at 550^{0}C the amount of cracking gases was 34% for HZSM-5 -containing catalyst as compared with 17.5% for the HY-containing catalyst. By the gasoline amount produced at 550^{0}C (17%) and light gas oil at 500^{0}C (37%) HY-catalyst is superior to HZSM-contact (9% gasoline and 30% light gas oil). Gasoline produced over the HZSM-5 catalyst characterized by higher octane number. The conclusion about the possibility of using Al(5.0)NaMM + HY- catalyst for the production of light products was made.



1-dioxide, 2-gasoline, 3-light gas oil, 4-the amount of light products

Figure 1 – The yields of VG PPCP basic cracking products on Al (5.0) NaMM + HY and Al (5.0) NaMM + HZSM-5 catalysts at 500°C and 550°C

The introduction of zeolites into pillared montmorillonite (Table 1) leads to an increase in total acidity from 195 μmol NH_3/g to 250 and 274 μmol NH_3/g for HY and HZSM-5 – containing catalysts, respectively. HZSM-5 zeolite catalyst is distinguished not only by high acidity, but also the highest (28%) content of strong acid sites responsible for increased gases formation.

Analysis of the hydrocarbon composition of gasoline (Table 2) shows that over HZSM-5 zeolite catalyst takes place considerable aromatization of hydrocarbons. Yield of aromatic hydrocarbons reaches 55.3% at 550^{0}C. Benzene quantity at this temperature is 7.9%. On HY –catalyst benzene does not formed with a total amount of aromatic hydrocarbons equal to 30.7%. Quantity of isoparaffins formed on HY catalyst on 4,8-3.3% over the former on HZSM -5 catalyst.

Table 1 - The acidity of the pillared AlNaMM, Al(5.0)NaMM+HY and Al(5.0) NaMM+HZSM-5 based catalysts according to the TPD of ammonia. Silica module of HZSM-5 is 29

Sample	Amount of acid sites	Acid sites			
		weak <200^{0}C	medium 200-300^{0}C	strong > 300^{0}C	Total acidity
Al(5.0)NaMM+ HZSM-5	%	40	32	28	100
	μmol NH_3/g	110	88	77	274
Al(5.0)NaMM+HY	%	45	30	25	100
	μmol NH_3/g	112.5	75	62.5	250
Al(5.0)NaMM	%	45	35	20	100
	μmol NH_3/g	88	68	39	195

Table 2 - Hydrocarbon group composition of gasolines cracking of VG PPCP over Al(5.0)NaMM + HY and Al(5.0)NaMM+HZSM - 5 catalysts

Hydrocarbon	Yield, wt%			
	Al(5.0)NaMM+HY		Al(5.0)NaMM+ HZSM-5	
	500^{0}C	550^{0}C	500^{0}C	550^{0}C
Paraffins	3.0	2.9	6.4	4.6
Izoparaffins	20.4	19.1	15.6	15.8
Olefins	16.3	19.3	26.7	9.7
Aromatics	32.8	30.7	35.2	55.3
Naphthenes	27.5	30.0	15.8	14.6
Oxygenates	0	0	0.2	0.2
Unknown	0	0	0	0

For carrying out the cracking process on petrochemical direction with increased yield of light alkenes bizeolite HY + HZSM-5 catalyst containing 15% HY- and 15% HZSM-5-zeolite with silicate module SiO_2/Al_2O_3 = 51 was synthesized. Tagan montmorillonite in Na-form and Al-pillared (Al(2.5)NaMM) used as a carrier. The weight ratio of HY and HZSM-5 - zeolites was 1: 1.

According to elemental analysis Na amount in the sample of Al(2.5) NaMM + HY + ZSM-5 catalyst was 0.58%.

Structural characteristics bizeolite Al (2.5) NaMM + HY + HZSM-5 - catalyst are shown in Table 3.

Table 3 - Structural characteristics mono (HY) – and bizeolite HY and HZSM -5-catalysts on Al (2.5) NaMM

Sample	$S_{уд}$,m^2/g	V_{max}, cm^3/g	R, Å	micropores,%	mesopores, %
Al(2.5)NaMM+ HY	149.3	0.101	10-70	37.7	62.3
Al(2.5)NaMM+ HY+HZSM-5	194.1	0.94	10-70	67.1	55.3

Bizeolite 15% HY + 15% HZSM-5/Al (2.5) NaMM - catalyst compared to 15% HY / Al (2.5) NaMM – catalyst differ high specific surface area and a larger number of micropores defined by narrowly porous HZSM-5 zeolite.

Basal reflex for Al (2.5) NaMM + HY + HZSM-5 is 14 Å, ie, increases for 2,1 Å, as for the Al (5.0)NaMM based samples, containing HY zeolite or HZSM-5 zeolite with a SiO_2 /Al_2O_3 modulus equal to 29.

Acidity spectrum of bizeolite Al (2.5) NaMM + HY + HZSM-5 catalyst is shown in Figure 2. The total acidity of the catalyst is 163.8 μmol NH_3 /g. The amount of the strong acid sites -7.6%,medium a.c. -46.9%,weak -45.9%.

Using narrowly porous HZSM-5 - zeolite with silicate module 51 in the composition of bizeolite containing catalyst on Al (2.5) NaMM - matrix reduces total acidity and increasing the number of weak and medium acid centers as compared with a zeolite catalyst HZSM-5 with a silica module 29 (Table 1).

The composition of the products formed in the cracking VG PPCP with end boiling 534^{0}C at different temperatures using the bizeolite catalyst containing narrowly porous HZSM-5 zeolite with silica modulus 51 is shown in Table 4.