The Application of Mechanochemical Technologies in Zeolite Catalysis

ALEXANDER V. VOSMERIKOV, LYUDMILA M. VELICHKINA, LYUDMILA N. VOSMERIKOVA,
LYUDMILA L. KOROBITSYNA and GENNADY V. IVANOV

*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademichesky 3, Tomsk 634021 (Russia)*

E-mail: dmps@ipc.tsc.ru

Abstract

The influence of mechanochemical activation (MCA) on physicochemical, adsorption, and catalytic properties of a zeolite in refining low-octane gasoline fraction and aromatization of propane-butane fraction is studied. It is shown that MCA of a zeolite leads to the decrease in its crystallinity degree, specific surface, and acidity. In the composition of the products obtained at the conversion of directly distilled gasoline fractions over activated catalysts the concentration of aromatic hydrocarbons decreases, the content of alkenes, naphthenes and isoalkanes increases, the yield of the desired product enhances. The yield of aromatic hydrocarbons during the conversion of C_3-C_4 saturated hydrocarbons over a zeolite catalyst subjected to mechanical activation for 12 h increases by almost 10 %, its life between regenerations is 1.5–2 times longer.

INTRODUCTION

Catalytic activity of high-silica zeolites of pentacyl type in the processes of raw petroleum conversion is due both to molecular-sieve and acidic properties. One of the ways to control them is mechanochemical activation (MCA). It allows one not only to update the methods for zeolite synthesis but also effectively improves operational characteristics of a zeolite [1–6]. This method does not exercise a negative influence on the environment because it gives no harmful sewage, unlike catalyst production by deposition. MCA nature is determined by defect formation at an intensive mechanical action on the solid body structure [1]. By varying the time and intensity of the action on a zeolite, one may purposefully change its operational characteristics. That is why our aim was to study catalytic properties of zeolite catalysts subjected to MCA of different intensity and for different periods of time in the process of refining directly distilled gasolines and aromatization of propane-butane fraction.

EXPERIMENTAL

High-silica zeolites ($SiO_2/Al_2O_3 = 60$) were produced *via* hydrothermal synthesis at 175 °C for 4–6 days from alkaline alumosilicagels using hexamethylenediamine as organic additive. The samples were decationized *via* double treatment with 25 % aqueous NH_4Cl solution at 90 °C for 2 h, then dried at 110 °C and calcined in air for 6 h (Na_2O content in H-ZSM-5 was less than 0.05 %). MCA treatment of the sample was carried out in ball vibrational and planetary mills. The operating load of the centrifugal planetary mill was 80 g, steel balls of 8 mm in diameter were used as milling bodies. Due to different mechanical actions, zeolite treatment period changed from 5 to 20 min in the planetary mill and from 6 to 96 h in the ball vibrational mill.

Crystallinity degree of the activated zeolites was calculated using IR-spectra, their specific surface was measured by chromatographic method using low-temperature argon adsorption. IR-spectra of the zeolites studied were recorded on Specord-75 IR spectrophotometer

in pellets with KBr (1.2 mg ZSM per 300 mg KBr in air). The quality of the obtained ZSM was estimated using their characteristic absorption bands. For example, an indication of the presence of zeolite phase is the absorption band at $550-560$ cm^{-1} related to the vibrations of the external bonds of AlO$_4$ and SiO$_4$ tetrahedrons and conditioned by the presence of doubled four-, five- and six-membered rings. The crystallinity degree of samples was determined using the ratio of the intensity of the band at 550 cm^{-1} to that of the band at 450 cm^{-1} [7, 8].

The acidic properties of the catalyst surface were tested using temperature-programmed desorption (TPD) of ammonia. The procedure of TPD experiments is described in [3]. The concentration of acidic sites in the samples studied was determined by the amount of ammonia that desorbs at the moment of recording desorption peaks and was expressed in micromoles per 1 g of the catalyst. The precision of gas-chromatographic determination of ammonia desorbed is 5 %. To calculate activation energy, ammonia desorption from the samples was carried out at different heating rates, namely, 5, 10, 15 and 20 °C/min. Activation energies were determined using the procedure described in [9].

Catalytic activity of the catalysts prepared was measured in a flow installation 5 cm^3 in volume with a stationary catalyst bed. The tests were carried at atmospheric pressure, reaction temperature and flow rate respectively $320-480$ °C and 2 h^{-1} in the process of conversion of a directly distilled gasoline fraction (I.B.P. − 180 °C) of a gas condensate; $400-600$ °C and $100-200$ h^{-1} in the process of dehydrocyclooli-

gomerization of a mixture of lower alkanes (ethane: 2.2; propane: 73.7; butanes: 24.1 mass %). The products were analysed by gas chromatography. Octane numbers of the raw material and catalyzates were determined by calculation (based on gas chromatography data) and by graphical method [10]. When determining the period of the stable catalyst operation in the process of C$_2$–C$_4$ alkanes aromatization, the tests were run continuously for several hours, the reaction products were analyzed at certain intervals that were equal for all the samples. The stability of the catalyst operation was assessed by the changes both in conversion degree of the raw material and selectivity of aromatic hydrocarbons formation.

RESULTS AND DISCUSSION

The studies performed have demonstrated that IR-spectra of MCA zeolite catalysts exhibit narrower adsorption bands and their better resolution, which is obviously connected with a finer dispersion of zeolites particles. A prolonged mechanical action on a zeolite results in its amorphization (Table 1). Crystallinity degree and specific surface of ZSM-5 change insignificantly with increasing activation time in the ball vibrational mill up to 48 h but further increase in activation period leads to a pronounced decrease in these indices. When activating ZSM-5 in the planetary mill for only some minutes, a drastic decrease both in crystallinity degree and specific surface proceeds. Thus, after 5 min activation the crystallinity degree decreases to 54 %, specific surface reduces almost 3 times. After activation for 20 min

TABLE 1

Characteristics of a zeolite subjected to mechanical activation over different periods of time

Milling method	Activation time	Crystallinity, %	Specific surface, m^2/g
Without milling	0	96	453
Vibrational mill	24 h	96	450
	48 h	91	420
	72 h	80	346
	96 h	61	199
Planetary mill	5 min	54	163
	10 min	31	78
	20 min	Amorphous	29

TABLE 2

Acidic properties of a zeolite catalyst subjected to MCA in a ball vibrational (hours) and planetary mills (min)

Activation time	T_{max}, °C		Concentration, mmol/g			E_{act}, kJ/mol	
	I	II	C_I	C_{II}	C_S	E_I	E_{II}
−	220	425	304	280	584	33.5	126.7
24 h	220	425	298	279	577	32.7	125.5
48 h	220	420	290	278	568	32.0	124.8
72 h	210	415	260	179	439	28.6	111.0
96 h	205	410	188	128	316	23.4	81.8
5 min	160	365	111	84	195	22.7	85.3
10 min	150	300	42	39	81	19.8	34.8
20 min	120	200	11	17	27	−	−

Note. T_I and T_{II} are the temperatures of the peak maximums for the forms I and II; C_I, C_{II} and C_S are the concentrations of acidic sites of forms I and II, and total concentration, respectively; E_I and E_{II} is the activation energies of ammonia desorption for forms I and II..

the adsorption bands characteristic of a zeolite phase are not observed in IR-spectrum, *i. e.*, the crystal lattice of ZSM-5 is completely destroyed.

Mechanochemical activation of a zeolite catalyst sufficiently influences its acidic properties (Table 2). All the samples subjected to the activation in the ball vibrating mill possess two types of acidic sites which is confirmed by the presence of two maximums on TPD curve: weak acidic sites characterized by ammonia desorption within 100−320 °C and strong acidic ones characterized by ammonia desorption within 320−600 °C. ZSM-5 treatment in the ball vibrational mill for the first 48 h insignificantly changes its acidity. The prolongation of the zeolite activation leads to a pronounced reduction both in acidic site concentration and strength, which is evidenced by a shift of the peak maximums into the region of lower temperatures, as well as to the reduction in activation energy of ammonia desorption. On ZSM-5 grinding in the planetary mill for even a short period of time a drastic drop in its acidity is observed. It is probable that mechanical action results in the destruction of the porous sample structure that leads to a decrease in quantity of active sites previously available for adsorbate molecules located in the pores and channels of a zeolite. Thus, zeolite activation in the planetary mill for 5 min (or in the

ball vibrating mill at the MCA period of not less that 48 h) pronouncedly changes its acidic properties.

The changes occurring in zeolite structure and acidity after MCA influence its catalytic characteristics. Table 3 gives the results showing the influence of the time and intensity of mechanical action on the catalytic zeolite activity in the process of refining a directly distilled gasoline fraction of gas condensate. MCA of a zeolitte catalyst leads to the decrease in its aromatizing activity. Over the zeolites subjected to mechanical action the catalysate yield is increased. Its octane number reduces insignificantly resulting from the redistribution of arenes and isolalkanes concentrations in the reaction products. In addition, in the catalysate obtained the content of benzene, the most toxic among the arenes, reduces and the fraction of *p*- and *m*-xylenes increases. These changes are the most marked over a catalyst activated for 72 h or more. Gaseous products contain principally low alkanes, among them propane and butane prevail. Zeolite MCA does not practically effect the composition of the gaseous products formed.

When applying the planetary mill, a stronger mechanical action on the porous zeolite structure takes place; as a result, acidic and catalytic properties of a sample change within a shorter activation period than in the vibration-

TABLE 3

Influence of ZSM milling time in the vibrational (hours) and planetary (min) mills on the catalysate composition ($T_p = 400$ °C, $W = 2$ h^{-1})

Catalyzate composition	Content, mass. %							Octane number	Catalyzate yield, %
	n-Alkenes C$_3$–C$_4$	Alkenes C$_3$–C$_4$	n-Alkanes C$_{5+}$	Isoalkanes C$_{5+}$	Napthenes alkenes C$_{5+}$	Alkenes C$_{5+}$	Arenes		
Directly distilled	–	–	23.4	41.5	24.3	–	10.8	51	
Without milling:	4.9	0.5	5.3	25.5	0.7	1.5	61.7	92	69
After milling for:									
24 h	10.2	0.8	4.6	23.5	1.0	1.6	58.3	92	65
48 h	10.4	0.8	4.6	25.4	1.8	1.8	55.2	91	73
72 h	8.8	0.5	4.4	28.7	2.5	1.6	53.5	90	75
96 h	7.7	1.2	5.4	32.0	3.4	2.8	47.5	87	79
5 min	8.3	1.0	5.4	32.5	2.2	2.7	48.0	88	75
10 min	6.2	2.4	11.5	36.2	9.4	5.8	28.5	78	80
20 min	2.2	0.6	24.0	38.3	15.7	2.1	17.1	56	95

al mill. ZSM-5 treatment in the planetary mill for 5 min leads to the same changes in the composition of the products as those caused by MCA in the ball vibrating mill for 96 h. Namely, the concentration of aromatic hydrocarbons decreases by 13.7−14.2 %, C$_{5+}$ isolakanes content increases by 6.5−7.0 %, the yield of gasolines with octane numbers of almost 90 units increases by 6−10 % (see Table 3).

The data given in Table 3 show that an optimum duration of zeolite MCA in the planetary mill is 5 min. Gasoline produced over this catalyst is characterized by an increased isoalkanes content (32.5 %) and a reduced content of aromatic hydrocarbons (48.0 %), its octane umber is 88 units. Gasoline produced over an inactivated catalyst under the same process conditions contains 25.5 % of isoalkanes and 61.7 % of aromatic hydrocarbons, its octane number (92) only slightly surpasses the octane number of the above gasoline.

Thus, MCA of a zeolite catalyst leads to a decrease in crystallinity degree, specific surface and acidity. MCA of a catalyst favourably influences the composition of the products formed in the conversion of directly milled gasoline fraction: the concentration of aromatic hydrocarbons decreases, the yield of gasolines with an increased C$_{5+}$ isoalkanes fraction rises. Catalytic properties of a catalyst crushed in the ball vibrating mill for 96 h only slightly differ from those of a zeolite activated in the planetary mill for 5 min.

A zeolite containing nanosized powder (NSP) of zinc as modifier was selected for the tests in the process of C$_2$–C$_4$ alkanes aromatization. Metal powder was produced in a laboratory installation using the method of wire electro-explosion under argon. The catalyst was prepared by dry mixing Zn and zeolite powder. Mechanochemical activation of a sample was carried out in the ball vibrating mill at room temperature for 6, 12, 18 and 24 h.

Table 4 represents the results for the influence of the period of mechanical grinding of 0.5 % Zn(NSP)/ZSM-5 on its catalytic activity and selectivity in the process of C$_2$–C$_4$ low-alkane aromatization. Mechanical activation for 6 h leads to a significant increase both in the catalyst activity (estimated as the transformation degree of the initial raw material) and its selectivity for the formation of aromatic hydrocarbons. A prolonged period of mechanical action on the catalyst (to 12 h) leads to a more significant rise in its aromatic activity at the initial process temperature. At 550 °C and volume rate 100 h^{-1}, the selectivity of aromatic hydrocarbon formation increases and reaches 59.2 %.

When the period of the sample grinding is prolonged to 18 h, its aromatic activity de-

TABLE 4

Influence of the grinding time of 0.5 % Zn(NSP)/ZSM-5 on the composition of the products of C_2–C_4 alkanes conversion

Grinding time	W, h^{-1}	T_r, °C	X, %	S_1, %	S_2, %	S_3, %	S_4, %	A, %
Without grinding	100	450	61	3.9	78.5	3.2	14.5	8.8
	100	500	88	4.3	59.2	1.7	34.8	30.6
	100	550	99	4.8	42.9	1.1	51.3	50.8
	200	600	95	6.6	44.7	3.3	45.4	43.1
6 h	100	450	66	3.2	53.4	2.9	40.5	26.7
	100	500	89	3.8	51.5	1.0	43.6	38.8
	100	550	99	5.7	42.2	0.9	51.1	50.6
	200	550	98	6.6	43.4	1.6	48.4	47.4
12 h	100	450	66	3.4	51.9	2.0	42.7	28.2
	100	500	93	4.3	50.9	1.0	43.8	40.7
	100	550	99	5.6	34.6	0.6	59.2	58.6
	200	550	98	6.0	43.2	2.0	48.9	47.9
18 h	100	450	68	3.6	56.2	2.5	37.7	25,6
	100	500	91	4.6	50.4	1.3	43.8	39.9
	100	550	99	5.4	41.3	0.8	52.5	52.0
	200	550	99	7.1	46.1	1.6	45.1	44.6
24 h	100	450	69	3.7	64.0	2.8	29.5	20.4
	100	500	86	4.4	58.4	1.4	35.7	30.7
	100	550	98	6.4	53.6	0.7	39.3	38.5
	200	550	97	7.2	49.2	2.8	40.9	39.7

Note. W is the volumetric rate; T_r is the temperature of reaction; X is the conversion degree; S_1, S_2, S_3 and S_4 are the selectivities of the formation of hydrogen, C_1–C_2 alkanes, C_2–C_3 alkenes and aromatic hydrocarbons, respectively; A is the yield of aromatic hydrocarbons.

creases as compared to the catalyst subjected to MCA treatment; however, it remains more active than a non-activated sample. A catalyst subjected to the grinding for 24 h is characterized by lower aromatizing activity as compared to other samples studied.

Table 5 shows the data on the influence of the grinding period of a 0.5 % Zn(NSP)/ZSM-5 on the yield of the desired product and the composition of gaseous and liquid products of C_2–C_4 low-alkanes conversion. The maximum amount of aromatic hydrocarbons is formed on 0.5 % Zn(NSP)/ZSM-5 subjected to MCA for 12 h being 58.6 %. On other samples, smaller amounts of aromatic hydrocarbons are formed, at the same time their contents remain high. With increasing time of catalyst grinding, the following regularity in the changes of the composition of liquid products formed is observed: benzene content increases, the con-

tent of C_8 and higher hydrocarbons decreases, toluene concentration changes insignificantly as compared to other aromatic hydrocarbons. The period of catalyst grinding insignificantly influences the composition of gaseous products. Thus, MCA of a Zn-containing catalyst influences principally the composition of liquid products, which is obviously connected with the changes in the dispersion degree and in the microporous zeolite structure. Zeolite pore size reduction under the action of external mechanical forces leads to diffusion complications connected with the limited possibility of penetration or formation in the pores as well as with hintered transport of large molecules, *e. g.*, alkylnaphthalene hydrocarbons, through zeolite channels. At the same time one may note that as a result of zeolite grinding for 12 or 18 h the concentration of active Zn^{2+}-containing sites available for the reacting molecules

TABLE 5

Composition of the products of C_2–C_4 alkanes conversion on 0.5 % Zn(NSP)/ZSM-5 subjected to grinding for different periods of time (T_r = 550 °C, W = 100 h^{-1})

Grinding time	Catalyzate yield, mass %	Composition of liquid hydrocarbons, mass %				Composition of gaseous hydrocarbons, mass %					
		Benzene	Toluene	C_8 aromatics	C_{9+} aromatics	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
0	50.8	31.9	39.4	11.4	17.3	9.8	60.1	2.0	25.9	0.2	2.0
6 h	50.6	30.4	37.9	14.3	17.4	11.3	54.9	1.7	29.9	0.2	2.0
12 h	58.6	38.7	32.1	8.7	20.5	13.3	53.9	1.2	29.0	0.2	2.4
18 h	52.0	40.0	37.9	6.5	15.6	11.0	57.9	1.5	27.3	0.2	2.1
24 h	38.5	41.7	36.9	5.9	15.5	10.2	57.2	1.0	28.1	0.2	3.3
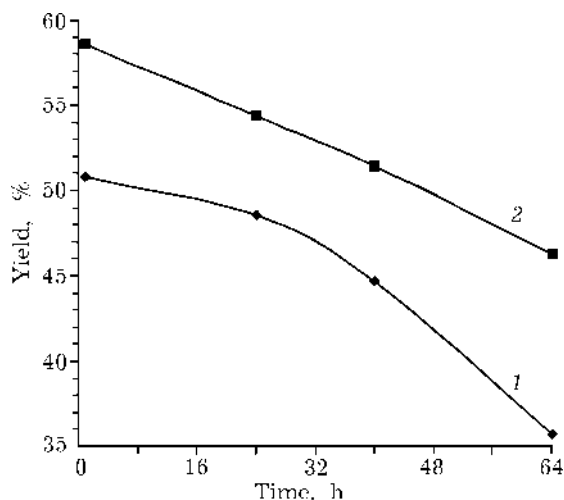
Fig. 1. The yield of aromatic hydrocarbons *vs.* operation time of 0.5 % Zn(NSP)/ZSM-5 (T_r = 550 °C, W = 100 h^{-1}): *1* – without grinding; *2* – grinding for 12 h.

increases which leads to the rise in its aromatizing activity.

A 0.5 % Zn(NSP)/ZSM-5 catalyst subjected to MCA for 12 h was tested for the period of stable work in the aromatization of C_2–C_4 alkanes (Fig. 1). Mechanochemical activation leads to the increase not only in catalyst activity, but to the increase of its stable operation time. During 64 h of its continuous operation the yield of arenes decreases by 13.8 % whereas the decrease is 15.1 % on a non-activated catalyst. In addition, during the whole reaction cycle, arene yield over an activated 0.5 % Zn(NSP)/ZSM-5 is significantly higher than over the initial sample. After 64 h operation, the catalyst keeps quite high aromatizing activity; that is why one may continue its further testing because it is possible to increase the period between the oxidative regenerations.

Thus, on the basis on the results obtained we may conclude that mechanochemical activation favourably influence catalytic properties of a zeolite containing 0.5 % Zn(NSP). Its grinding in a ball vibration mill for 12 h leads both to the increase in the activity, selectivity and stability of the catalyst in the process of C_2–C_4 alkanes aromatization.

CONCLUSIONS

Significant changes in crystallinity degree, specific surface and acidity of a zeolite catalyst occur at its activation in the planetary mill

within 5 min and the ball vibrational mill within 48 h. In the composition of the products formed at the conversion of a directly distilled gasoline fraction over an activated zeolite the concentration of aromatic hydrocarbons decreases, the contents of alkenes, naphthenes, and isoalkanes as well as of gasoline yield increase. Activity and operation stability of 0.5 % Zn(NSP)/ZSM-5 in the aromatization of C_2–C_4 low alkanes improve after its mechanochemical activation in the vibrational mill. Catalyst MCA within 12 h allows increasing the yield of aromatic hydrocarbons by almost 10 %, its life between regenerations exceeds 60 h. The 0.5 % Zn(NSP)/ZSM-5 catalyst not only preserves its catalytic properties after mechanical activation for at least 18 h but these properties are even improved. This evidences that catalytic properties of 0.5 % Zn(NSP)/ZSM-5 found under laboratory conditions should not be sufficiently changed during its full-scale operation including transportation, loading into reactor, oxidative regeneration, *i. e.* various external mechanical actions.

Acknowledgements

REFERENCES

1 R. A. Buyanov, *Khim. prom-st'*, 3 (1996) 151.
2 E. G. Avvakumov, Mekhanokhimichesky sintez v neorganicheskoy khimii, Nauka, Novosibirsk, 1991.
3 A. V. Vosmerikov, V. I. Erofeev, *ZhFKh*, 69 (1995) 787.
4 A. V. Vosmerikov, L. M. Velichkina, A. I. Vagin, *Nefte-pererabotka i neftekhimiya*, 2 (1999) 30.
5 G. S. Khodakov, *Uspekhi khimii*, 32 (1983) 860.
6 E. G. Avvakumov, *Chemistry for Sustainable Development*, 2 (1994) 475.
7 A. A. Kubasov, K. V. Topchieva, in.: Sovremennye problemy fizicheskoy khimii, Izd-vo MGU, Moscow, 1975, vol. 8, p. 309.
8 N. S. Khashgul'gova, T. V. Limova, S. N. Khajiev *et al.*, *Vestn. MGU. Ser. 2. Khimiya*, 20 (1979) 544.
9 J. Tomas and W. Tomas, Heterogeneous Catalysis, Academic Press, London – New York, 1967.
10 S. I. Kolesnikov, I. M. Kolesnikov, *Neftepererabotka i neftekhimiya*, 6 (1996) 30.