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Acidic and Basic Properties of Zeolite-Containing Cracking Catalyst in the Process of Butene-1 Isomerization

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Abstract—The process of butene-1 isomerization in the presence of two groups of samples of zeolite-containing catalyst (ZCC) that earlier participated in the traditional and oxidative catalytic cracking of vacuum gasoil is investigated. It is established that the nature of the reaction mixture and conditions of the cracking process are key factors in forming the acidic and basic properties of the catalyst. It is shown that the highest activity in the butene-1 isomerization into *cis-/trans*-butene-2 is demonstrated by ZCC samples that participated in the oxidative catalytic cracking (oxycracking). It is suggested that the enhanced catalytic activity of this group of ZCC samples was related to the availability of acid–base centers in the form of radical-like oxygen along with protic- and aprotic-type acidic centers in the structure of the oxidative compaction products.

Keywords: zeolite-containing catalysts, acidic-basic properties, isomerization, oxycracking, products of oxidative compaction.

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INTRODUCTION

Zeolite containing catalysts (ZCCs) play an important role in development of petrochemical processes. They provide the basis for the production of effective catalysts for processing petroleum fractions, synthesis gas conversion, solving problems of ecological catalysis, and so on [1–12].

Improvements in ZCCs that enhance their activity, selectivity, and stability facilitate the development and increased efficiency of technological processes. For example, the evolution of the industrial cracking catalyst of high-boiling petroleum fractions now allows us to produce high-quality automotive gasoline, and to provide a reliable base of raw materials for the petrochemical industry [7, 8, 13–15]. The future pace of catalytic cracking development depends on our successfully resolving problems related to the processing of heavy crude oil, which impose stricter requirements upon the catalytic and operational characteristics of ZCC.

Industrial catalysts of the KMTs series; LYuKS, Adamant, and bizeolite cracking catalysts with the low-modulus additive IK-17-1 (based on ZSM-5-type zeolite); and others must be included among the successful developments in the recent years [16–19].

Earlier, we conducted comparative studies of the traditional and oxidative catalytic cracking (oxycracking) of vacuum gasoil in the presence of oxygen, using bizeolite cracking catalyst with IK-17-1 additive [20–22]. A substantial difference between the catalytic activity of catalysts of one structural type and chemical composition during traditional oxidative catalytic cracking (oxycracking) was established from a comparison of the process parameters. In our opinion, the reason for this phenomenon lies in oxygen affecting changes in the acid–base properties of the ZCC.

In this work, we present results on the activity of ZCC samples taken after participating in the traditional and oxycracking of gasoil during the isomerization of butene-1 into *cis-/trans*-butene-2. The catalytic and acid–base properties of the samples are compared.

EXPERIMENTAL

The process of catalytic cracking in the presence and absence of oxygen was conducted in a flow reactor with a packed bed of Grace industrial zeolite-containing catalytic cracking catalyst OMNIKAT-340. A low-modulus zeolite of the ZSM-5 type (zeolite IK-17-1, manufactured by OAO NZKhK) was used as an additive. Zeolite additive IK-17-1 was introduced into the base catalyst by mechanical mixing [23, 24] in the amount of 3 wt %. Techniques for conducting traditional and oxidative cracking were described in [20, 21].

The specific surface area of the initial and nonregenerated samples after participating in cracking was determined from the low-temperature absorption of nitrogen at 77 K by means of BET. The samples were preliminarily evacuated (10–5 mm Hg) for 5 h at 350°C. According to BET, the specific surface area (S_{sp}) of the OMNIKAT industrial catalyst was 200 m^2/g. The bulk density (ρ_{bulk}) was 0.65 g/mL, and the pore volume (V_{pore}) was 0.4 mm^3/g. These parameters for the IK-17-1 were $S_{sp} = 300$ m^2/g and $\rho_{bulk} = 500$ kg/m^3. The components were mixed in a vibrating ball mill for 1 h with subsequent calcination at 550°C for 6 h. A technological additive was added to the catalyst at the stage of component mixing, facilitating the formation of water vapor, strengthening the catalyst, and assisting the process of granule formation [25].

Butene-1 isomerization was conducted using a laboratory flow unit with a stationary catalyst layer at 300°C and atmospheric pressure. Butene-1 was produced directly in the setup via the dehydration of *n*-butyl alcohol on aluminum oxide pretreated with a 0.05 wt % solution of KOH (to suppress double bond migration). The volumetric flow rate of the initial butene-1 was 240 h^{-1}.

Chromatographic analysis of the butene isomer composition was conducted on a CHROM-5 chromatograph equipped with a thermal conductivity detector. A column packed with Inza brick INZ-600 support modified with 15% mineral oil was used. The column length was 3 m. The detector current was 60 mA.

The catalyst's activity was characterized on the basis of the degree of butene-1 conversion relative to the surface area of the catalyst.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a NETZSCH instrument. A linear polythermal regime of heating at a rate of 10 K/min in air was selected for our analysis.

RESULTS AND DISCUSSION

It is known that the activity and selectivity of catalysts are directly related to their acidity [26–30]. Various techniques are used for determining the nature, number, and strength of acidic centers in catalysts: the temperature-programmed adsorption–desorption (TPD) of gaseous bases, amine titration, NMR, the IR spectroscopy of adsorbed molecules, and others. In addition, the possibility of a relationship between the acidic properties of aluminosilicate catalysts and the activity in the isomerization reaction of hydrocarbons has been shown by a number of authors [26–32].

In order to compare the dynamics of changes in the acidity of the ZCC, samples were selected that had already been used in cracking and differed by the length of time they were subjected to the process (15, 30, 45, 60 min) and the conditions of catalytic cracking: four samples had already been used in the oxycracking and four samples had participated in traditional nonoxidative catalytic cracking.

The data presented in Table 1 indicate that the ZCC samples of the same composition but different in the conditions of cracking operated as different catalysts: the degree of butene-1 transformation in the presence of samples that had participated in cracking under traditional catalytic conditions were lower than for the respective samples that had participated in oxycracking. However, the substantial differences were not obvious at first. For example, the degrees of butene-1 isomerization in the presence of samples that had participated in both types of cracking for 15 min (samples 1CC и 1OCC) were very close, but the considerable difference between then became apparent after 30 min of operation (samples 2CC и 2OCC): the activity of 2OCC fell by 1.1, and 5.5% in the case of 2CC. This trend was even more pronounced the longer the catalysts were subjected to cracking conditions.

The following series was obtained when the activity of the tested samples in the isomerization of butene-1 into *cis-/trans*-isomers of butene-2 were compared:

1 OCC > 2 OCC > 3 OCC > 1 CC > 2 CC > 4 OCC.

The dependences of the conversion of the vacuum gasoil and the distribution of compaction products during catalytic cracking with and without oxygen are presented in Fig. 1. It can be seen that the degree of petroleum fraction conversion grew by 14% under conditions of oxycracking, compared to the traditional regime. This effect indicates that oxygen is a significant promoter of the process. The similarity between the general patterns of the activity of the ZCC samples

Table 1. Characteristics of our samples of zeolite-containing catalysts

Sample	t, min	S, m^2	S_{sp}, m^2/g	x, %	A, m^{-2}
	Before catalysis	654.13	202.5	–	–
		Traditional catalytic cracking			
1 CC	15	628.2	188.8	39.4	0.061
2 CC	30	603.8	175.1	34.9	0.058
3 CC	45	–	–	29.0	–
4 CC	60	–	–	18.6	–
		Oxidative catalytic cracking			
1 OCC	15	598.3	164.8	39.0	0.065
2 OCC	30	585.7	159.8	37.9	0.064
3 OCC	45	582.5	156.0	36.9	0.063
4 OCC	60	524.7	147.9	19.6	0.030

t is the length of time spent under conditions of catalytic cracking; *S* is the surface area; S_{sp} is the specific surface area; *x* is the degree of butene-1 conversion; *A* is activity.

Table 2. Characteristics of exothermic effects from the data of differential thermal analysis

Sample	Regime	t, min	T_{max}, °C			Δm, %	Δm_{tot}, %
			start	maximum	end		
1 OCC	Oxidative	15	250.4	398.6	672.1	2.5	12.2
			173.6	485.2	575.7	9.7	
2 OCC	Oxidative	30	274.5	404.5	624.7	4	15.05
			304.5	503.9	574.4	11.05	
3 OCC	Oxidative	45	280.7	407.5	675.9	3.5	14.9
			250.3	503.7	582.8	11.4	
4 OCC	Oxidative	60	274	404.6	814.6	4	16.16
			284.2	504.1	588.4	12.16	
1 CC	Nonoxidative	15	354.7	525.5	682.7	2.58	2.58

Δm is mass loss; Δm_{tot} is total mass loss. The rest of the denotations are the same as in Table 1.

during oxycracking and the subsequent process of butene-1 isomerization in their presence can also be seen. This is even more surprising when we consider that according to the data of thermal analysis, the amount of compaction products (CP) formed under identical conditions of the oxidative catalytic cracking of vacuum gasoil is higher than under the conditions of traditional nonoxidative cracking (Table 2, Fig. 1), and the activity of ZCC under oxycracking conditions was also higher than under nonoxidative conditions [20, 21].

According to the literature data [33–35], the ratio of *cis-/trans*-isomers allows us to suggest one possible nature of the acidic centers. Based on this concept, we analyzed the ratios of *cis*- and *trans*-butene-2 yields for the ZCC samples, depending on the regime of their participation in the cracking process (Fig. 2). The presented dependences are of a notable antisymbatic character. Comparative analysis of the obtained graphic dependences showed that the reaction medium, and not the duration of the cracking process, affected the *cis-/trans*-butene-2 ratio the most. In addition, this dependence for the samples that had participated in the traditional catalytic cracking process (Fig. 2, curve *1*) was more gradual and almost linear (approximate level of significance, $R = 0.97$). The concentration of either protic or aprotic acidic centers fell sharply as the duration of the ZCC samples' exposure to the conditions of traditional cracking grew, due likely to the accumulation of surface products of the reactions of oligomerization, polymerization, and condensation.

The dependence of the *cis-/trans*-butene-2 ratio on the duration of the oxycracking process (Fig. 2, curve *2*) is more complicated and changes almost exponentially. Two time intervals can be identified in this dependence that differ significantly in character: in the initial time period (15 min), the ratio of *cis-/trans-* isomers is characterized by notable dominance of the *cis*-butene-2, followed by a minimum (30 min) after which the sec-

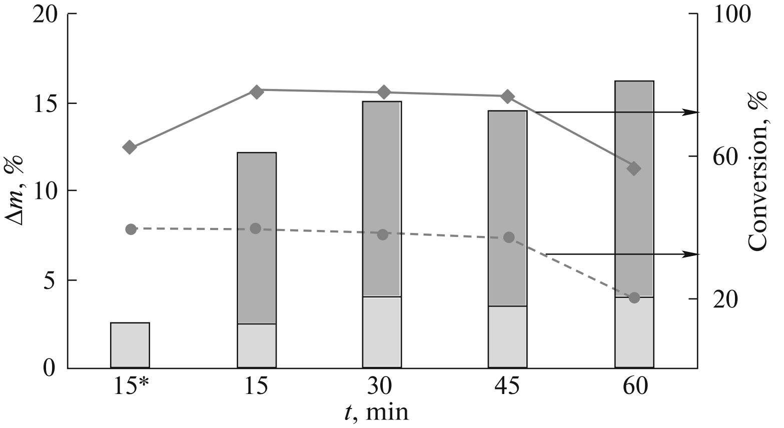

Fig. 1. Effect of the duration of the oxycracking process on the conversion of vacuum gasoil (solid line), butene-1 (dashed line), and the dynamics of mass accumulation and loss for endoeffects: T_{max} = 398–407, 485–504°C. 15* is the sample from oxycracking for 15 min at T_{max} = 525°C, where T_{max} is the temperature of the maximum of the exothermic effect.

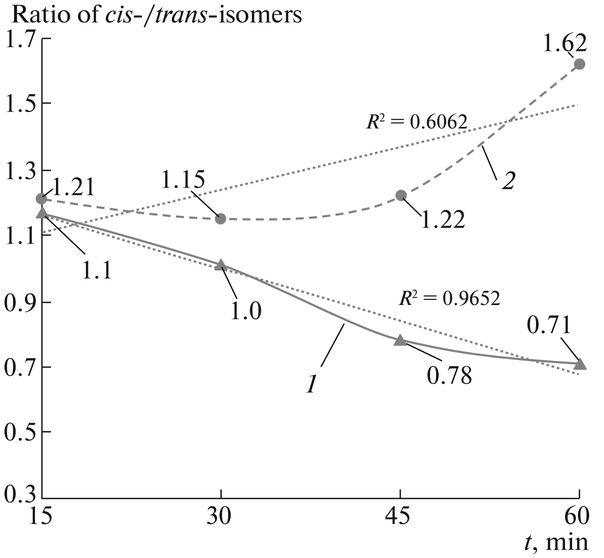

Fig. 2. Dependences of *cis-/trans*-butene-2 ratio in the presence of the catalyst samples that had already participated in (*1*) traditional and (*2*) oxidative catalytic cracking on the duration of the process.

tion of a resumed substantial increase in the *cis*-butene-2 yield is observed. In our opinion, the nonlinearity of this dependence is related to the development of the oxycracking catalyst, which is accompanied by a change in the acid–base properties of the catalyst in the presence of oxygen.

It was also noted that for both groups of the ZCC samples with the shortest length of stay in the cracking zone, the dependences are characterized by fairly high contents of *trans*-butene-2. The relatively high concentration of protic centers responsible for the *trans*-stereospecificity observed for the samples subjected to traditional cracking was due to the requirements on this type of industrial catalyst [17, 18, 33, 34], for which the protic acidity due to the availability of surface OH-groups responsible for the protonation of both alkanes and olefins is fundamental [2–4]. The observed fast deactivation of the group of samples subjected to traditional cracking suggests that most of the protic centers in the ZCC were on the outer surface of the zeolite, since the sizes of the initial butene-1 and the *cis-/trans*-isomers of butene-2 molecules are very close and much smaller than the diameter of channels in the zeolite.

Compared to these samples, not only was there no drop in the isomerization activity of the ZCC for the oxycracking samples in which the surface fraction of protic centers fell almost immediately; it actually grew, due to formation of *cis*-butene-2.

The ratio of butene-1 to *trans*-butene-2 is another important indicator of the contribution from protic acidic centers to the general acidic and basic properties observed for the catalysts during the process of butene-1 isomerization (Fig. 3). Once again, the medium in which the catalytic cracking was conducted made the main contribution: the samples that had participated in the process of oxycracking were characterized with higher contents of not only *cis*- but also *trans*-butene-2. The experimental dependences also displayed high levels of significance (R = 0.95–0.98).

Since it was established for the samples subjected to traditional cracking that the ratio of the formed *cis-/trans*-butene-2 and butene-1/*trans*-butene-2 was close to 1 in the course of butene-1 isomerization, it is

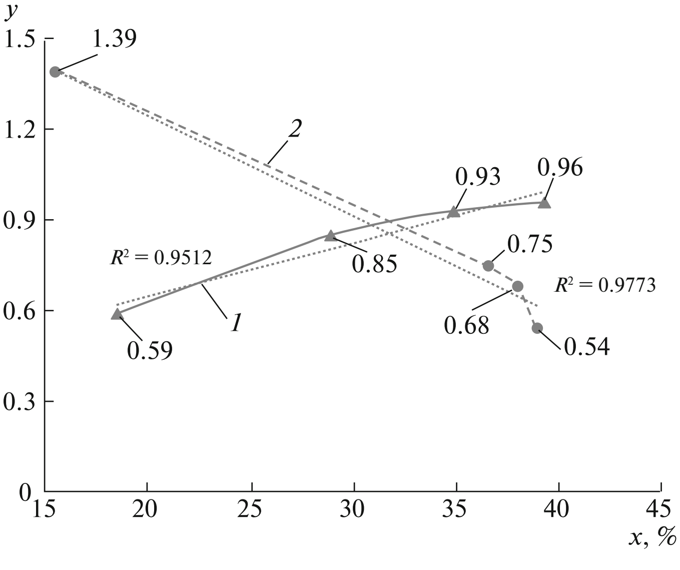

Fig. 3. Dependences of the ratio of butene-1 to *trans*-butene-2 (y) in the presence of catalyst samples that had already participated in (*1*) traditional and (*2*) oxidative catalytic cracking on the degree of butene-1 isomerization (x).

worth noting that *n*-alkene activation was accompanied by the formation of side products (carbocations) in the first minutes of the isomerization process. Carbocations are very active particles that react with adsorbed particles at exceptionally high rates, resulting in the accumulation of tightly adsorbed, high molecular weight structures on the surface of a catalyst, thereby increasing the carbonization of the surface, blocking the aprotic active centers of the catalyst, and thus reducing olefin conversion and catalyst activity for a short period of time.

Analysis of dependences of the ratio of butene-2 isomers produced during butene-1 isomerization in the presence of ZCC samples that had participated in the oxycracking process suggests that the acidic and basic properties of these samples were determined not only by the protic acidic centers of the catalyst samples but by their basic centers as well. The availability of such centers follows from the clearly pronounced *cis*-stereospecific isomerization of butene-1. The formation of this type of isomer is likely related to the availability of Lewis acidic centers [29, 34, 35]. On the other hand, the high degree of carbonization of the samples subjected to oxycracking casts some doubt on their contribution in this particular case. It follows that other active centers prone to display electron acceptor properties participated in the activation of the initial olefin. Since the enhanced isomerization activity observed in our studies correlated with the activity in the process of oxycracking, we assume that the structural features of this type of active centers were based on their having emerged and evolved under the influence of the reaction medium and oxygen. The nature of these centers is as yet unknown, but we speculate that carbonate and carboxylate oxycomplexes form in the process of oxycracking, and in turn form products of oxidative compaction (POC) on a catalyst's surface.

The catalytic activity of POC has been verified experimentally a number of times [32, 36–39]. In addition, the availability of the atomic O^- anion-radical, which according to present concepts plays a key role in a number of processes of oxidative catalysis, is not inconceivable [4, 40–45]. The oxygen atom in the POC composition displays high affinity toward electrons and is therefore capable of polarizing the double bond in butene-1 and playing the role of a basic center.

The data from thermal analysis also indicate the products of compaction that formed on the ZCC samples during both types of cracking differ in structure. The sample subjected to traditional cracking for 15 min was characterized by the presence of a single exothermic peak with a maximum at 525.5°C. The samples that had already participated in the process of oxycracking for 15–60 min displayed two exothermic peaks with maxima at 398–407 and 485–504°C, respectively (Table 2, Fig. 1). The observed 40–125°C reduction in the maxima of exothermic peaks indicates that the POC formed during oxycracking is different, i.e., less condensed.

Further investigation of the location of the stabilization and coordination environment of oxygen is required in order to fully understand the mechanism of hydrocarbon activation with the participation of such centers, and the possible role of radical-like oxygen in the process. The authors plan to conduct such a study in the future.

CONCLUSIONS

The results obtained in our investigation of butene-1 isomerization show that the formation of *cis-/trans*-isomers of butene-2 in the presence of samples that had already participated in the process of traditional catalytic cracking occurs with the participation of protic acidic centers. It was established that the higher isomerization ability of the samples that had already participated in the process of oxycracking was due to changes in the structure of active centers, particularly the formation and participation of surface oxygen centers embedded in the structure of the products of oxidative compaction. Our conclusions on the change in the nature of the active centers of ZCC samples allows us to explain the enhanced activity and stability of the samples that had already participated in the process of oxycracking and butene-1 isomerization.

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