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# Coking Mechanism and the Distribution of Agglomeration Products in High-Silica MFI-Type Zeolites

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# Abstract

Currently there is no agreement among the researchers worldwide about the mechanism of MFI-type zeolites deactivation due to coke accumulation in the areas of coke localization. This problem does not allow answering the question about the stability of these zeolites and their resistance to the reversible deactivation by coke. Our research provides the solution to this problem using physical and chemical methods: the electron paramagnetic resonance, X-ray photoelectron spectroscopy, thermal analysis and catalytic method of methanol conversion into hydrocarbons. We show that the key mechanism of coke formation is carbenium mechanism. Deactivation of zeolites occurs mainly due to the coke accumulation on the external surface of crystals of MFI-type zeolites. The contribution of "hydrocarbon pool" mechanism is negligibly small compared to the contribution of the carbenium mechanism of olefin formation by the dehydration reaction. This understanding allows increasing the stability of MFI type zeolites to coke formation by removing the acidic centres from the external surface of the crystals.

Keywords: coke formation, MFI-type zeolites, carbenium mechanism, zeolites stability

## INTRODUCTION

It is known [1-4] that the high-silicon MFItype zeolites differ from the zeolites of other types (X, Y, mordenite, erionite, *etc.*) by the increased resistance to coking in catalytic conversion of methanol and olefins or other reactions. The increased stability of MFI-type zeolites is explained by the fact that the coke is formed only on the external surface of the crystals [1]. Another research [2] suggests that the coke can also be formed inside the zeolite channels. However, this coke should be different from the regular coke due to the steric constraints. It could be a product of low-molecular olefins polymerization.

The process of converting methanol into hydrocarbons is a complex sequence of the reactions: dehydration of methanol into dimethyl ether (DME) and ethylene; oligomerization, cyclization and alkylation of olefins; cracking of heavy olefins, and the reallocation of hydrogen [5-7]. It is shown [5, 8] that deactivation of the catalyst in relation to deep methanol transformation occurs earlier than the deactivation in relation to methanol dehydration into DME. The differences in the kinetics of deactivation are due to the fact that deep methanol transformations occur mainly at the active sites within the zeolite channels while the rapid conversion of methanol into DME takes place at sufficiently weak acid sites both inside the channels and on the external surface of the crystals. This is confirmed by the blockage of internal volume of crystals by coking [9, 10] that results in the decrease of the fraction of deep methanol transformations while DME is formed at the weak sites of the external surface until its complete poisoning.

At the time, the explanations of coke formation were based on carbenium ion theory and radical theory [11, 12]. Carbenium ion has high reaction capacity, but its stability is so low that its existence cannot be detected by any of the existing physicochemical methods. Carbenium ions which can lead chain ion polymerization or condensation are usually formed on the acid type catalysts [13]. On the other hand, free radicals are formed during the adsorption of hydrocarbons on MFI-type zeolites [14–16]. However, it is noted [17] that the radicals appear only in the presence of trace amounts of oxygen in the system, probably, due to the presence of specific radical-forming oxygen-containing centres in the catalyst. It is shown [18-20] that the adsorption of hydrocarbons on zeolite systems is accompanied with the formation of radicals which can be detected by the electron paramagnetic resonance (EPR).

The formal scheme of coke formation involves the formation of coke directly from methanol and olefins. The formation of coke from other hydrocarbons is neglected since their coking rates are low [11]. Intermediate active particles of radical nature are formed on some catalyst sites. These particles rapidly interact with the reaction products through a radical chain mechanism and, as a result, turn into large aromatic radicals. They are stabilized in the intercrystalline space or on the external surface of the crystals blocking the internal volume of the zeolite. However, at the present time, the science community [12] is against the radical mechanism. Coking of olefins is predominating through the carbenium ion mechanism at low temperature [21]. Coking occurs by the addition of the carbenium ion to the coke agglomerate fixed to the active site of the external surface. Therefore, the rate of zeolite deactivation for this mechanism depends on silicate module on the external surface of zeolite  $(M_{ext})$ .

Another important discussion relates to the localization and mechanism of deactivation of MFItype zeolites. The methods of infrared spectroscopy and electron spectroscopy of diffuse reflectance (ESDR) demonstrate [22, 23] that coking of H-zeolites with high silica content (MFI) at the temperatures up to 400 °C occurs by the carbenium ion mechanism inside zeolite channels. Other studies demonstrate, using the methods of poisoning the external surface with trimethylpyridine during the olefin oligomerization process, that coking at the temperatures below 250-280 °C occurs on the external surface of the zeolite [1, 14, 15, 24]. There is the third opinion on the localization of coke formation: the coke is formed both inside the zeolite channels and on the external surface of the zeolite [25–28]. Therefore, the literature does not provide clear answer to the question of the localization of coke formation.

Many authors claim that the main mechanism for methanol conversion and further coke formation is the formation of ethylene from lower methylbenzenes in the channels of MFI with subsequent remethylation, and a cycle of methylation-cracking consisting only of  $C_{3+}$  olefins [29, 30]. Along with that, polymethylbenzenes are the primary products of the methanol conversion [31, 32]. In addition to the mechanisms described above, the most popular is the parallel formation of the C-C bond, represented as the "hydrocarbon pool mechanism" [30, 33-38]. The authors show that the reaction occurs through the alkene and arene cycles. It has been claimed that, for the arene cycle, olefins are formed due to the growth of the side chain of polymethylbenzens (the so-called side chain-mechanism) or reduction in the number of carbon atoms in the aromatic ring (the paring mechanism). Carbenium ions can be considered as important hydrocarbon pool species [35].

Thus, there are three generally recognized facts on coke formation during methanol conversion into hydrocarbons:

- First, it has been largely proven that coke is formed on the external surface of crystals or in the pores between crystals.

- Second, there are two conventional mechanisms of coking: low-temperature and high temperature, which differ from each other in the properties of the coke formed, dependence of deactivation rate on temperature and, probably, the nature of the coking agent.

– Third, the ratio of two mechanisms depends on the temperature as well as the properties of the catalyst itself: the size of the crystals and the silicate module on the external surface of the crystals ( $M_{ext}$ ).

Thus, despite the controversy over the process of MFI-type zeolites coking found in the literature, it is necessary to explain all experimental results from a common point of view, and we propose such explanation.

## MATERIALS AND METHODS

To study the nature of coking processes on MFI-type zeolites, we used EPR, X-ray photoelectronic spectra (XPS), thermal analysis and catalytic method.

The methanol conversion into hydrocarbons is exothermic process which is characterized by frontal development of the catalyst layer [39-41]. Three reaction zones can be distinguished in the catalyst layer: I zone is the zone of exhausted (totally poisoned) catalyst; **II zone** is the zone of the main reaction and heat dissipation; **III zone** is the zone of the catalyst, which has not yet been reached by the main reaction, partially deactivated by the products of reaction. The first zone is characterized by the fact that the main reaction front has passed through it already; the catalyst located in this zone is completely deactivated. Only methanol and dimethyl ether can work as coking agents in this zone for a fully deactivated catalyst during the reaction. In the second zone (the zone of increased temperature), olefins, aromatic hydrocarbons, and partly methanol and paraffins can work as coking agents. The third zone is characterized by low temperature. The possible coking agents are aromatic and paraffin hydrocarbons, as well as olefins in small concentration.

Our express method for determining catalytic stability [40] was used to determine the rate of zeolite deactivation by coke. This method is based on overlapping the heat dissipation front appearing in the catalyst layer and the front of zeolite deactivation by coke. Therefore, the rate of zeolite deactivation by coke (U) was determined by the speed of the heat dissipation front across the catalyst layer under stationary reaction conditions. It was measured in grams of a catalyst deactivated in a time unit:

# $U = \Delta L / \Delta \tau$

where U is the deactivation rate – the amount of catalyst completely deactivated by coke per time unit (integral characteristic);  $\Delta L$  is the part of catalyst layer measured in grams, to which the heat dissipation zone has moved for the time  $\Delta \tau$ .

The temperature distribution across the catalyst layer was measured with a movable thermocouple, which was moved periodically along the reactor axis. Two types of reactors with different diameters were used.

The methanol load and the linear velocity of the reaction mixture along the cross section of the reactor remained the same. The methanol conversion to hydrocarbons was carried out in flow mode at a volumetric rate of liquid methanol of 2 h<sup>-1</sup>. MFI-type zeolites with the molar  $SiO_2/Al_2O_3$  ratio ranging from 38 to 200 synthesized by different methods were investigated. The catalyst was coked in the methanol conversion to hydrocarbons

at atmospheric pressure and within temperature range of 375-520 °C.

For EPR measurements, the samples of zeolites were either coked during the time in which the same part of the catalyst layer lost its activity, or the samples coked during the same amount of time were compared. We investigated the samples taken from the first and third zones. The samples from the first zone lost their activity and were called coked or completely deactivated. Samples from the third zone did not lose their activity and were called partially deactivated. The EPR spectra were detected using the JES-3BX at both 300 and 77 K. Coked and partially deactivated samples were pre-vacuumed at 90 °C to the residual pressure of  $10^{-2}$  Torr. To determine the concentration of paramagnetic centres (PMC) in the samples, the reference  $VOSO_4 \cdot 9H_9O$ with the known PMC concentration was used.

Thermal analysis of the samples was performed on the derivatograph Q-1500 D in a dynamic mode in an air atmosphere with a heating rate of 10  $^{\circ}C/min$ . The samples were placed on plates.

The specificity of the agglomeration products distribution in different samples of MFI type zeolites was also studied by low-temperature adsorption of argon on fresh and coked samples. The zeolites were coked either under model conditions on the Ugine Eyraud Setaram microbalance in excess of ethylene in the gas flow  $(0.4 \text{ L/(min \cdot g of catalyst)})$  at 380 °C, or in the flow reactor during methanol conversion to hydrocarbons. Ethylene was used as a coking agent since it is an intermediate in methanol conversion to hydrocarbons, and it contributes mostly to the total coking process. After coking, the samples were purged in the nitrogen stream at a temperature of 380 °C for 30 min. Argon adsorption isotherms were measured in vacuum adsorption equipment with microbalance MTB - 10<sup>-8</sup> Setaram. The samples were pre-degassed in a vacuum for 5-6 h at 300 °C. The analysis of the isotherms of argon adsorption allowed calculating the volume of intercrystalline micropores, the external surface of crystals as well as its variation depending on the coke content.

X-ray photoelectronic spectra (XPS) were recorded on the ultra-high vacuum electron spectrometer VG ESCA-3 (Vacuum Generators, Great Britain) using  $AlK_{\alpha}$  radiation ( $E_{h\nu} = 1486.6$  eV). The powder samples were fixed to the holder with double-sided adhesive tape. After vacuuming to a residual pressure of 10 Torr, the over-

view spectra of the surfaces of the samples at the binding energy range of 0-1000 eV as well as the spectral regions of Al2*p*, Si2*p*, C1*s*, O1*s* were recorded. The position of the lines was calibrated against the peak Si2*p* which has a binding energy of 103.5 eV [41]. The method described in [42] makes it possible to determine the Si/Al ratio on the surface of the samples (in this case the thickness of the examined layer is 25-30 Å).

# **RESULTS AND DISCUSSION**

MFI-type zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio ranging from 38 to 200 as determined by chemical analysis were investigated. The XPS data show that the same series of zeolites had silicate module on the external surface of the crystals  $(M_{ext})$  in the range of 50 to 700. The value of  $M_{ext}$  depends on the method of zeolite synthesis as well as the pretreatment conditions. The EPR spectra for the coked samples vary significantly. The EPR spectrum of coked zeolite with M<sub>ovt</sub> of 50 is the superposition of two signals: a broad signal (6.7 G), which is quite difficult to isolate, and a narrow one (3.2 G). After opening the vial in the air, the narrow signal disappears completely (the broadening of the narrow signal with increased oxygen pressure has been specially checked), and the intensity of the broad signal decreases with no changes in its width. The EPR spectrum of the coked sample with  $M_{ext}$  of 120 is a broad signal with  $\Delta H$  of 10.5 G, and its intensity decreases slightly with adsorption of atmospheric oxygen. Further increase of M<sub>evt</sub> up to approximately 160 results in the narrowing of EPR signal (Fig. 1).

The EPR spectrum of the coked zeolite with  $M_{ext}$  of 170 is the superposition of broad (6.5 G) and narrow (4.2 G) signals with its inherent changes at oxygen adsorption. With further increase of  $M_{ext}$ , the spectrum becomes more uniform: the intensity ratio of broad and narrow signals changes towards the predominance of the narrow signal, which is further narrowing. For example, for the coked sample with  $M_{ext}$  of 600, the EPR spectrum represents almost solely a narrow signal (3 G). When oxygen is adsorbed, the narrow signal disappears, and only the broad signal with very low intensity (7.5 G) remains in the spectrum.

As it is seen from the general picture of the change in the width of EPR signal for coke sediments depending on the molar  $SiO_{9}/Al_{2}O_{3}$  ratio

on the external surface of zeolite crystals, three regions of EPR signals for coke sediments are observed (see Fig. 1).

In zones I ( $M_{ext} < 50-60$ ) and III ( $M_{ext} > 170$ ), the superposition of the two signals is observed, and in zone II ( $M_{ext}$  of 60–170), the EPR spectra consist of one broad signal with decreasing intensity as oxygen is adsorbed. It should be noted that so far only the completely coked samples taken from zone I were discussed. The EPR spectra of partly deactivated samples taken from zone III (see Fig. 1) consist of the broad signal (11–11.5 G) with decreasing intensity as oxygen is adsorbed.

Let us assume that under the reaction conditions described above (standard conditions for methanol conversion to hydrocarbons), coking agents and coke precursors are formed at the active sites located inside the zeolite channels. The formation of condensed coke structures with polyaromatic flat nets occurs at the active sites located on the external surface of the crystals (in secondary pores). We also assume that the active site includes at least one aluminium atom (or more). The following picture of zeolite coking will be obtained.

The condensed coke agglomerate grows on each active site located on the external surface of zeolite crystals. In this case the external surface is defined as any surface of the zeolite crystals outside the zeolite channels (the size of which is about 6 Å). At the same time, the zeolite channels



Fig. 1. The width of the predominant EPR signal for coked zeolites depending on the silicate module on the external surface of zeolite crystals. x = the narrow signal in the zone I.



Fig. 2. The scheme of coke accumulation on MFI-type zeolites [43].

are being gradually blocked by the coke growing on the surface. The channels are filled with reaction products and coke precursors which do not provide ERP signal. Filling of the blocked channels with the organic products should reduce the free volume of zeolite pores. When the coke agglomerates growing on the external surface overlap and block most of the external surface, the main part of the active sites in the volume of the zeolite channels is switched off from the reaction due to their filling with the reaction products. The formation of hydrocarbons is stopped with complete zeolite deactivation. Further increase in the coke amount on such zeolite can, probably, occur only due to coke alkylation with methanol. The less active sites on the external surface (above  $M_{ext}$ ), the larger the surface per active site, the more coke can be formed on one site until the zeolite is completely deactivated, and the longer the catalyst operates under the same reaction conditions (Fig. 2).

It should be noted that the steric restrictions do not allow the formation of non-desorbed compounds, which block the active sites in the volume of zeolite crystals, inside the channels of MFI zeolites. If the external surface of the zeolite crystals would be free of active sites, the MFI-type zeolites would almost never get coked. Taking into account that MFI-type zeolites are coked as described above, the results obtained for the first time by M. Guisnet et al. [44] become understandable. Investigating the composition of coke deposits in zeolites the authors determined that agglomeration products extracted from zeolite by dissolution of the zeolite framework are highly alkylated mono- and biaromatic compounds. Based on this, the authors claimed that the coke in MFItype zeolites is formed at the intersection of channels over the entire volume of crystals while

each "coke molecule" neutralizes one active site. It is clear that mono- and biaromatic compounds cannot irreversibly adsorb in the channels of MFI-type zeolites. They can only fill these channels without being able to leave them due to the coke blocking of pore mouths on the external surface of crystals.

Apparently, in the zones II and III of the  $M_{ext}$ values (see Fig. 1), the active sites are uniform and evenly distributed. At low  $\mathbf{M}_{\mathrm{ext}}$  values (the beginning of zone II), when the surface is blocked, the size of coke agglomerates stuck together is small, the C/H ratio is low, and the EPR spectrum shows a broad signal from single paramagnetic centres that weakly interact with each other. In this case, the intensity of the EPR signal decreases with the increase in the quantity of adsorbed oxygen (one oxygen molecule "kills" one PMC). Signal width is mainly conditioned by the hyperfine structure (HFS) from H coke nuclei while the unpaired electron of PMC is delocalized in a system of conjugate rings of this nucleus. As the number of active sites on the external surface decreases ( $\mathbf{M}_{ext}$  increases), the size of individual coke agglomerates stabilized on one active site of a fully deactivated sample increases. At the same time, the degree of polycondensation of coke sediments as well as C/H ratio increases. As a result, the broad signal is narrowed since the HFS from protons decreases due to the decline of the hydrogen amount in the system and the increase in the area of delocalization of the unpaired electron.

Another mechanism for narrowing EPR signal can be the exchange narrowing, which also implies increase of the delocalization areas of the unpaired electron, *i. e.*, degree of polycondensation. Hence the increased sensitivity of the signal to oxygen adsorption becomes clear: the larger the delocalization area of the unpaired electron, the greater the probability of its interaction with adsorbed oxygen, and the greater the drop in the intensity of EPR signals. Finally, at some value of  $M_{ext}$ , the size of coke agglomerates and, respectively, the C/H ratio become so large that the conductivity electrons can appear in the system. At the same time, narrow signal is formed in a fully cooked sample. The sensitivity of this signal to oxygen is caused by the exchange of conductivity electrons between the carbon nets and the adsorbed oxygen. Further  $M_{ext}$  increasing results in enlargement of coke agglomerates with C/H ratio that leads to an increase in the number of conductivity electrons and the narrowing of the signal due to exchange between the PMC.

Thus, from the available experimental data, it is possible to estimate the critical size of polycondensation areas at which the narrow signal appears in EPR spectra. If we estimate the projection area of aluminium-oxide or silicone-oxide tetrahedron to the surface of the zeolite, the maximum area it occupies on the surface at any location of the tetrahedron will be 3.5 Å<sup>2</sup>. The  $M_{ext}$ appropriating to the appearance of the narrow signal is 170-180, which corresponds to Si/Al of 85-90. The area of the carbon ring in the polycondensed system is  $3.6 \times 3.0$  Å<sup>2</sup>. Based on these data, the number of rings of polycondensed net of carbon deposits should be 36-40 while the linear size of such net should be about 19-20 Å. This size is well matched with the data on the pyrolysis of carbon systems at a temperature above 600 °C, when the narrow signal usually appears [45].

In the zone I (see Fig. 1), at low  $M_{ext}$  values (< 50-60), the active sites are apparently nonuniform and unevenly distributed. The EPR spectra for the samples in this zone, as well as in the zone III, show the superposition of narrow and broad signals due to appearance of active sites with several aluminium ions  $Si(OAl)_n$  (n > 1) at small M<sub>ext</sub> [46, 47]. The coking reactions also occur on these sites, possibly at a different rate. Appearance of  $Si(OAl)_n$  (n > 1) leads to a highly uneven distribution of active sites on the surface, which can result in the emergence of large areas free of active centres on the external surface. Thus, there is a probability that the coke agglomerate will grow at a complex active site. The size of the agglomerate can reach 19–20 Å even before the surface is completely blocked. This is a reason of appearance of the narrow signal in EPR spectra in this case. It should be noted that, all other things being equal, the time of complete coking of a zeolite is proportional to M<sub>evt</sub>.



Fig. 3. The maximum exceffect of coke burning in partially deactivated samples depending on the silicate module on the external surface of zeolite crystals.

Further it was observed that the width of the EPR signal for coke sediments in partially deactivated samples of the same zeolite series remained almost unchanged (from 11 to 11.5 G) throughout the  $M_{out}$  interval (see Fig. 1). At first glance, the independence of the EPR signal width from  $M_{avt}$ in partially deactivated samples indicates the same degree of coke sediments condensation. However, thermal analysis showed that this was not the case. In general, with an increase in  $M_{evt}$ , the maximum of exothermic effect of coke burning is shifted to the higher temperatures (Fig. 3). This fact indicates that condensation degree of coke deposits, *i. e.* C/H ratio, increases with  $M_{ext}$  raise in partially deactivated samples at similar deactivation degree of the samples (that was provided by experiment conditions), although the width of the EPR signal remains constant.

Although the width of EPR signal in partially deactivated samples remains insensitive to the  $\boldsymbol{M}_{\rm ext}$  variation, the dependence of its intensity on oxygen adsorption differs. Table 1 shows that, as  $M_{ext}$  grows, the sensitivity of the signal to oxygen increases due to the increasing polycondensation, and C/H ratio in coke. It has been previously pointed out that carbon deposits in MFI-type zeolites have a structure of condensed carbon nets similar to graphite. As long as individual coke agglomerates are not interconnected, there is no electronic gas, and the width of EPR signal remains almost constant. In this case, the width of the line will be determined by the degree of condensation of carbon deposits (C/H ratio). While coke agglomerates are separated from each other, the degree of its condensation is only appearing

TABLE 1

Sample	Coking	M <sub>ext</sub> , mol	Coked		Partially deactivated		$I_{\rm vac}/I_{\rm air}$
	time, h		Coke content, wt. %	$PMC \cdot 10^{-18},$ spin/g	Coke content, wt. %	$PMC \cdot 10^{-18}$ , spin/g	
1	24	50	9.0	4.1	2.5	3.8	2.5
2	10	120	5.6	4.7	2.1	5.0	1.5
3	24	300	7.2	3.0	1.7	3.3	3.5 - 4.0
4	50	600	5.9	1.6	0.9	1.7	5.5
5	0.5	600	0.7	1.5	0.5	1.6	3.7
6	70	700	5.6	1.2	0.8	1.0	6.0 - 7.0

Coke content, concentration of paramagnetic centres (PMC) and relative drop of EPR signal in the air in coked and partially deactivated samples

in the drop of the intensity of EPR signal during oxygen adsorption.

As  $M_{ext}$  increases, the distance between the active sites on the external zeolite surface as well as the growing coke agglomerates increases. Thus, the time of zeolite coking until the loss of activity also increases. The size of coke agglomerates in partially deactivated samples increases as well. This explains the shift of the exoeffect maximum to the high-temperature region of coke burning.

Aluminium atoms appear to be included in the structure of an active site, which drives the reactions of adding the next carbon rings to the coke agglomerate, and acts as coke stabilizer. Previously we have proposed the scheme for the growth of coke agglomerates on the external surface of zeolite crystals with the corresponding change in the strength of the acidic sites [48]. According to this scheme, the coke particle enhancement occurs by the addition of subsequent carbon atoms from the active site on the external surface of the zeolite, similar to the intercalation of olefin on the metal-carbon bond during the polymerization process.

During the methanol conversion to hydrocarbons in the steady state mode, the first coke portions are formed from aromatic hydrocarbons at the end of the catalyst layer in the hydrogen redistribution reaction zone. Coke is produced simultaneously on all aluminium ions on the external surface of the crystals, giving one PMC at each ion. The rate of coke formation from aromatic hydrocarbons is very low and does not determine the rate of zeolite poisoning. As soon as such partially deactivated zeolite is approached by the main thermal zone, the rate of coke formation increases due to the higher temperature and the changes in the nature of coking agents since the concentration of olefins is high in the main reaction zone. The rate of coke formation

from olefins determines the rate of zeolite deactivation, all other things being equal. At the same time, the coke amount in the zeolite increases while there is no formation of new PMCs, which is confirmed by the data in Table 1: the number of PMCs in coked and partially deactivated zeolites is the same. Moreover, the specially conducted experiments have shown that all PMCs are formed at the first moments of the process. Coking the sample for 0.5 and 50 h does not cause a change in the number of PMCs (samples 4 and 5, see Table 1) while the amount of coke deposited on the zeolite varies by the order of magnitude. The growing coke agglomerates on the crystal surface gradually block the channel entries, which results in filling the zeolite channels with "agglomeration products", reducing the free volume of zeolite channels, and contributing to the total amount of coke, determined by the thermal gravimetric analysis. These "agglomeration products" do not form PMCs.

In the zones II and III (see Fig. 1), the number of PMCs is proportional to the number of aluminium atoms on the external surface that indicates the involvement of each external aluminium atom in the formation of PMCs. Moving to the zone I (see Fig. 1), the proportionality is disrupted. The number of PMCs should increase while it slightly decreases (see Table 1). This fact confirms once again the above assumption of diversity of active sites in MFI-type zeolites at  $M_{ext} < 50-60$ . Apparently, in this zone there are Si-2 and Si-3 centres in the zeolite, having two or three aluminium atoms in the second coordination sphere of silicon atoms. These atoms are colocated and contribute to the formation of one PMC in coke agglomerate growing at the centre. Some texture characteristics for the original samples are given in Table 2. The number in the sample symbol corresponds to the molar SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

TABLE	2			
Texture	characteristics	of	the	samples

Sample	V, mmol/g	$W_0^{}$ , mmol/g	$a_{\rm m}^{\rm BET}$ , mmol/g	$W_0^{}/a_{ m m}^{ m BET}$	$(S\xi_{\rm m}+V)/W_0$	$R_{_{ m e}},\%$
Z-38	5.03	6.10	_	-	0.94	90
Z-51	4.09	4.81	4.58	1.05	0.95	85
Z-100	5.30	5.47	4.47	1.22	0.97	100
Z-135	5.54	5.72	5.08	1.12	0.98	95
Z-200	4.40	4.56	4.90	0.93	0.98	100
Z-50-1	4.02	4.44	_	-	0.96	90
Z-50-2	4.30	4.62	_	-	0.98	90

*Note.* V and  $W_0$  are the adsorption volume of the micropores calculated by the comparative method and the Dubinin–Radushkevich equation, respectively;  $a_m^{\text{BET}}$  is the monolayer capacity determined chromatographically by argon thermal desorption; S is the mesopores surface calculated by the comparative method;  $\xi_m$  is value of argon adsorption on the internal surface with monolayer argon covering ( $\xi_m^{\text{Ar}} = 9.44 \text{ mmol/m}^2$ );  $R_e$  is the degree of crystallinity.

ratio (module). Table 2 shows that the  $(S\xi_m + V)/W_0$  ratio is close to 1.0 (error is 6 %). The  $W_0/a_m^{\rm BET}$  ratio is maintained around 1.0 for all coked samples. Thus, formally the values of  $a_m^{\rm BET}(S^{\rm BET})$  and  $W_0$  for MFI-type zeolites are determined as the actual sums of adsorption volumes on the external surface of the crystallites and in its micropores, respectively.

Figure 4, *a* shows the dependence of the coke-free fraction of the intracrystalline volume  $1 - \theta = V_{\theta}/V^0$  (where  $V^0$  and  $V_{\theta}$  are volumes of the cavities of the original and coked samples, respectively) on the specific content of coke (*X*, g/g of the original zeolite) for the coked samples. We studied the Z-50-1 and Z-50-2 samples with close values of their external surface (*S* = 24 and 28 m<sup>2</sup>/g, respectively), the same silicate module (chemical analysis), and significantly different in stability during the methanol conversion to hydrocarbons. The Z-50-1 and Z-50-2 samples work stable for 500 and 200 h, respectively. For the

Z-50-1 sample, the volume of the intracrystalline space remains constant with an increase in coke to X of 0.05–0.06 g/g (see Fig. 4, *a*). Further increase of X leads to the proportional reduction in the volume of available micropores. For the Z-50-2 sample, linear decrease of  $V_{\rm \theta}$  is observed over the entire interval of coke accumulation values.

The maintenance of the  $V^0$  value for the Z-50-1 sample (as it is getting coked) can be explained by coke deposition exclusively on the external surface of the crystals while for the Z-50-2 sample it is possible that agglomeration products and coke are deposited on the external surface of the crystals and within the volume of micropores. The coke distribution on several zeolites with different silicate module (see Fig. 4, *b*) was investigated in more detail. It can be seen that the deposition of the same amount of coke on the samples results in different changes in the available volume of micropores. For the Z-200 sample, the value of  $V^0$  remains almost constant while it lin-



Fig. 4. Dependency of free in-crystalline volume on coke content: samples Z-50-1 and Z-50-2 (*a*); samples Z-200; Z-51; Z-38; Z-135; Z-100 (b).

early decreases with the coke content for all other samples. The linear plots of the curves are described by the equation:

 $\theta = \zeta X / (\rho_c V^0)$ 

where  $\rho_c$  is the coke density,  $\zeta$  is the degree of intracrystalline pores filling, the coke content.

According to earlier EPR data, the Z-200 sample contains high-condensed coke, while the remaining samples contain predominantly low-condensed coke. IR-spectroscopic data indicate that low-condensed agglomeration products consist of one-dimensional aromatic rings (the system with conjugated  $\pi$ -bonds). Based on geometric modelling, the limit density of such coke as benzene ring systems filling the zeolite channels was estimated as ρ of 1.43 g/cm<sup>3</sup>. Placing CH=CH groups between aromatic rings allows decreasing the density of such coke to 0.7-0.8 g/cm<sup>3</sup>. In any case, the density of such coke should be significantly lower than that of the conventional condensed coke  $(1.7-1.9 \text{ g/cm}^3)$ . Assuming that in the Z-135 sample the whole amount of coke is located inside the crystals,  $\rho_c$  is equal to 1.31 g/cm<sup>3</sup>, which is consistent with the above values. Other samples differ slightly in the density of coke or its distribution, *i. e.*, the "external" coke to "internal" coke ratio. Similar results were obtained for the distribution of coke formed during the methanol conversion into hydrocarbons.

Thus, it was established that the coke in MFItype zeolites (the products which cannot be desorbed at reaction temperature) can be located both in the volume of zeolite crystals and on the external surface of crystals. The method of direct measurement of coke distribution along with other methods can be used to study the reasons for the deactivation of zeolite catalysts.

Based on the density of the coke  $(0.7-1.43 \text{ g/cm}^3)$  which is formed within the zeolite channels it is claimed that this product can hardly be called "coke". These products containing 1-2 aromatic rings, in principle, must be desorbed from the active sites of zeolite, when the channel mouths are not blocked.

Comparing the results obtained by the method described above with the results obtained by other methods on the same zeolites, the following conclusions can be made. According to the values of silicate modules on the external surfaces, the zeolites are in a sequence of Z-100 < Z-35 < Z-51 < Z-50-1 < Z-200. These zeolites are in the zones II and III (see Fig. 1) on the general picture of the change in the width of EPR signals of coke deposits depending on the silicate module on the external surface of the zeolite crystals. The coke burning temperature measured by differential thermal analysis as well as the coke condensation leading to the deactivation of zeolites increases in the same sequence. It is important to note that samples Z-38 and Z-50-2 are in the zone I (see Fig. 1) in which the distribution of active sites on the external surface of the crystals is uneven. Consequently, in general, the fewer active sites on the external surface of zeolite crystals, the smaller the slope of the curve on Fig. 4, and the longer the stable section on the curve, *i. e.* the smaller the degree of reduction in the available internal volume at the same coke content in the zeolite. Thus, these data confirm the previous pattern of coke accumulation in MFI-type zeolites. The accumulation of coke on the external surface of crystals is the primary process which determines the deactivation of zeolites. Agglomeration products fill the internal volume by blocking the mouths of zeolite channels with the coke growing on the surface. With high density of the active sites on the external surface, this happens almost immediately when a small amount of coke accumulates in the zeolite. As the number of active sites on the external surface of the crystals decreases, the slope of the curve decreases, then the linear stable section appears with its following increase (see Fig. 4), i. e. the blocking of the mouths of zeolite channels begins later and later. Thus, the catalytic stability of zeolites is increased.

The contribution of the "hydrocarbon pool" mechanism to the decontamination of MFI-type zeolites by coke deserves a special mention.

The  $\psi$  value is called Thiele modulus  $\psi$  (psi) =  $[2k_{\text{chem}}/(D(A) \cdot R)]^{1/2} \cdot L$ where  $k_{\text{chem}}$  is the chemical reaction rate constant, *D* is the diffusion coefficient, *R* and *L* are the pore radius and length.

The Thiele modulus is dimensionless. It includes the geometric characteristics of the pore and the ratio of the chemical reaction rate constant to the diffusion coefficient. This parameter allows estimating the contributions of reactions occurring both inside the zeolite channels and on the external surface of the crystals, since it takes into account reaction rate coefficients, diffusion coefficients, the size of the pores of the catalyst and their length. In the case of rapid diffusion (meso- and macro-pores, internal kinetic diffusion), the Thiele modulus should be small D(A) >> k, ....

$$\psi = [2k_{\text{chem}}/(D(\mathbf{A}) \cdot R)]^{1/2} \cdot L \ll 1$$

Otherwise, when diffusion is a slow process (molecular diffusion within zeolite channels and pores), Thiele modulus becomes significant:  $D(A) \leq c h$ 

$$\begin{split} D(\mathbf{A}) &<< k_{\mathrm{chem}} \\ \psi &= [2k_{\mathrm{chem}}/(D(\mathbf{A})\cdot R)]^{1/2} \cdot L >> 1 \end{split}$$

The ratio of the reaction rates in the secondary porosity and in the zeolite channels will determine the predominant reaction mechanism. The values of diffusion coefficients in secondary porosity (external surface of crystals) are  $10^{-3-}$  $10^{-4}$  m<sup>2</sup>/h, which is 5–6 orders of magnitude higher than the values of diffusion coefficients in zeolite channels. This means that even if the external surface is only 1 % of the total surface, the amount of reagent passing through the secondary porosity in one unit of time will be 3–4 orders of magnitude higher than the value amount of reagent passing through the secondary porsity in the value of the amount of reagent passing through the secondary passing through the volume of zeolite channels.

Even if all the above-mentioned mechanisms for the conversion of olefins and methanol as well as coking occur, at best, the contribution of the "hydrocarbon pool" mechanism will be less than 0.1 %, *i. e.*, negligibly small compared to the contribution of a sequential mechanism, for example, the carbenium mechanism of olefin formation by the dehydration reaction.

#### CONCLUSION

The coke distribution on several zeolites with different silicate module was investigated. There is different tendency in coke formation for the Z-50-1 and Z-50-2 zeolites with silicate module 50 prepared by different methods. For the Z-50-1 zeolite at the beginning of coking the coke is disposed only on the external surface of the crystal while for the Z-50-2 agglomeration products and coke are deposited on both external surface of the crystals and the volume of micropores. On the other hand, the available micropore volume remains practically constant with increase of coke content on the Z-200 zeolite with the highest silicate module. All other samples show decrease in this value. It can be explained by the fact that the Z-200 sample contains high-condensed coke, while the remaining samples contain predominantly lowcondensed coke. The sequence of the zeolites by the values of silicate modules on the external surfaces  $(M_{evt})$  is Z-100 < Z-135 < Z-51 < Z-50-1 < Z-200. It is shown by EPR and thermal analysis data that the coke condensation leading to the deactivation of zeolites increases in the same sequence. Thus, the fewer active sites on the external surface of zeolite crystals, the smaller the degree of decrease in the available internal volume at the same coke content in the zeolite. The coke accumulation on the external surface of crystals of MFI-type zeolites is the primary process which determines the deactivation of zeolites. Filling of the internal volume by "agglomeration products" occurs by blocking the mouths of zeolite channels with the coke growing on the surface. Thus, the catalytic stability of zeolites is increased with a decrease in the number of active sites on the external surface of the crystals due to slower blocking of the mouths of zeolite channels. The values of diffusion coefficients on the external surface of crystals are higher than the values of diffusion coefficients in zeolite channels. This means that the amount of reagent passing through external surface of crystals in one unit of time will be higher than the amount of reagent passing through the volume of zeolite channels. Thus, the contribution of the "hydrocarbon pool" mechanism will be less than 0.1 %, *i. e.*, negligibly small compared to the contribution of the carbenium mechanism of olefin formation by the dehydration reaction.

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