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DRIVING FORCES OF COKE ALTERNATE DYNAMICS IN ZEOLITE DEACTIVATED

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An attempt has been made to treat oscillatory dynamic phenomena in zeolites on the base of participating the cluster species of the peculiar thermodynamic characteristics in direct and reverse processes. These characteristics are defined by the fact that the bulk phase exceeds any cluster phase of the same substance in high temperature region for the chemical potential value by $\Delta\mu$ causing the oscillatory dynamic phenomena in zeolite systems due to fusion of clusters into the bulk phase and bulk phase dissociation to clusters, repeated cluster fusion and so on. $\Delta\mu$ value is shown to be a driving force of both direct and reverse processes.

When transforming the organic compounds over solid catalysts, there is always formation and retention of heavy side-products either in the catalyst pores or on the external surface of catalyst micro crystals or in both these positions simultaneously. The formation of these non-desorbed products, generally called as coke, is the object of a range of studies and publications. A lot of physical, chemical and physicochemical methods are using for this purpose [1]. After the results obtained, the coke is shown to be not completely immobilized by the zeolite structures but demonstrates some dynamics. In particular, the coke issue from the zeolite pores onto external surface has been revealed. Nevertheless, a number of the questions concerning the coke behavior in the samples deactivated remains as not enough cleared queries. New experimental methods seem to be as promising ones in this connection.

Not long ago a new method for coke studies has been developed [2], the discrete-successive coke micro oxidation (DSCM) method. It consists in the successive giving the separate oxygen pulses (1 cm^3) at 500°C onto the placed in microreactor (system of gas chromatograph) zeolite catalyst coked sample (93 mg). For each oxygen dose the quantities of formed CO_2 and H_2O are determined (thermal conductivity detector), whence the carbon and hydrogen are calculated. As a result, coke burning dynamics and H/C value change in dependence of oxygen

number are got, i.e. the weight and the elemental composition of coke burned for each oxygen pulse are determined. Such a technique allows oxidizing the coke successively starting from the external surface of zeolite crystals and passing gradually to the coke in the pores. Precise analysis of experimental data permits to distinguish not only the external surface and inner pore coke but to discern locating of the latter between the separate zeolite structural elements also. As to the H/C value, it has been found in the main causes to be near the null, i.e. the coke formed under DSCM method conditions seems to be practically the pure carbon.

Recently [3] HZSM-5 sample deactivated in *n*-hexane aromatization has been studied using the abovementioned method. A new phenomenon has been revealed: the coke has been found to exist in the state of continual motion along the direction in turns towards the external surface of zeolite crystals as well as into the bulk of zeolite structure.

Fig. 1 gives the evidence of nothing else as of the coke dynamics in the deactivated sample during its aging with the vector directed by turn now onto the external surface of zeolite crystals, now within the deep of zeolite structure.

One can make not very difficult calculation. The zeolite powder assumed to be consisted from the cubic micro crystals with the ribs of $1 \mu\text{m}$. Assuming further the zeolite true density as 2 g/cm^3 , it is easy to calculate that zeolite of

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0.093 g of the masse contains $4.65 \cdot 10^{10}$ microcrystals of the above dimension. The surface of this crystal number makes up $2.79 \cdot 10^{19} \text{ \AA}^2$.

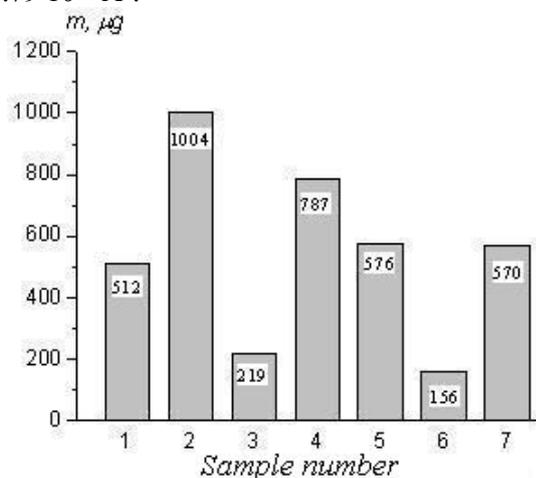


Fig. 1. Quantities of external surface coke for fresh deactivated (1) and aged during 64, 99, 204, 294, 295 and 296 days (2–7) samples of HZSM-5

Basing on the above data (Fig. 1), we will come from the zeolite external surface coke of 570 µg. This coke mass contains $2.85 \cdot 10^{19}$ carbon atoms. Carbon atom diameter is 1.54 Å [4]. On the zeolite surface each carbon atom occupies the square ground of the same rib dimension, i.e. 2.37 \AA^2 , while the total surface under $2.85 \cdot 10^{19}$ carbon atoms makes $6.75 \cdot 10^{19} \text{ \AA}^2$. When we divide the last value by the value of surface of total crystals in 93 mg of zeolites ($2.79 \cdot 10^{19} \text{ \AA}^2$), we obtain the value of 2.42. The last figure is the carbon monolayer number when external surface coke makes 570 µg. But from the Fig. 1 one can see that the external coke may be of essential greater magnitude. Therefore the average number of carbon mono layers on the external zeolite surface we assume as three layers.

Hence, the coke deposits on the deactivated catalyst would be in the continuous dynamics of alternate direction. In the literature [1] one can meet, as already abovementioned, the information concerning the escape of such deposits from within of the zeolite pore structure towards the external surface, but we did not meet any information about the reverse, all the more their reiterative dynamics.

The revealed phenomenon of coke oscillatory dynamics need the answer a question concerning the driving forces of the direct and

reverse processes as well as concerning the nature of the switching mechanism. In order to give such answer we will use the ideas of coke in bulk and cluster phases. In the case of full enveloping zeolite microcrystals by the coke, the latter will be considered as coke bulk phase independent from the envelop monolayer number, whereas the coke as a separate clusters on the same external surface of the microcrystals will be thought as coke cluster phase. The response to the above questions should be searched in the difference of fundamental physicochemical coke properties in these two phases.

This difference can be reflected by the consist pattern of relative change of the pressure values over the substance in the bulk and cluster phases shown in Fig. 2 [5, 6] in consideration of the proportionality change of saturated vapor value and chemical potentials of any substance in the form of the following equation:

$$\Delta\mu = RT \ln p_1/p_2, \quad (1)$$

where $\Delta\mu$ is the chemical potential change during the substance transfer from phase 1 of p_1 pressure towards the phase 2 of p_2 pressure, T is thermodynamic temperature, R is gas constant.

Let us to mark the coke chemical potentials in bulk and cluster phases at 500 °C as μ_b and μ_c . In accordance to the above consist pattern [5, 6], in the region $T > T_0$ such inequality

$$\mu_b > \mu_c \quad (2)$$

is valid due to the greater saturation pressure over the massive carbon phase than over the carbon cluster phase.

For the μ_b and μ_c ratio, the bulk multilayer coke (Fig. 3, a) would be thermodynamically unstable relatively the cluster coke and would trend to the transfer in the cluster state. The easiest way towards the transfer is decreasing of the external surface layer at the expense of penetrating the zeolite pores. Value $\Delta\mu$ characterizes the driving force of this transfer.

Such a transition will results in the gradual transfer of external surface carbon layer to monolayer (Fig. 3, b), originating someone of the graphene type, i.e. the monolayer carbon film which will fit close to zeolite crystal, still being characterized by chemical potential μ_b and thus by the ability to the further transition inside the porous structure. But now straight away the integrity of monolayer will be disturbed which

will result in its fragmentation, and the separate fragments will roll themselves into separate clusters (Fig. 3, c) with the chemical potential sharp decrease: μ_b jumpy will turn into μ_c .

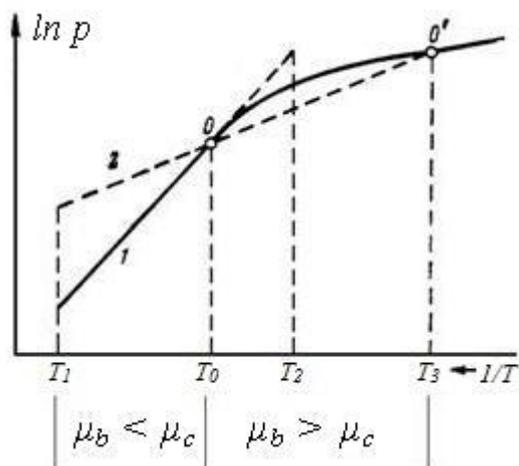


Fig. 2. Temperature dependence of saturated vapor over substance in the bulk phase (1) and in the cluster phase (2) in $\ln p-1/T$ coordinates

But penetrating the external surface coke in the porous zeolite structure occurs at μ_b , and thus

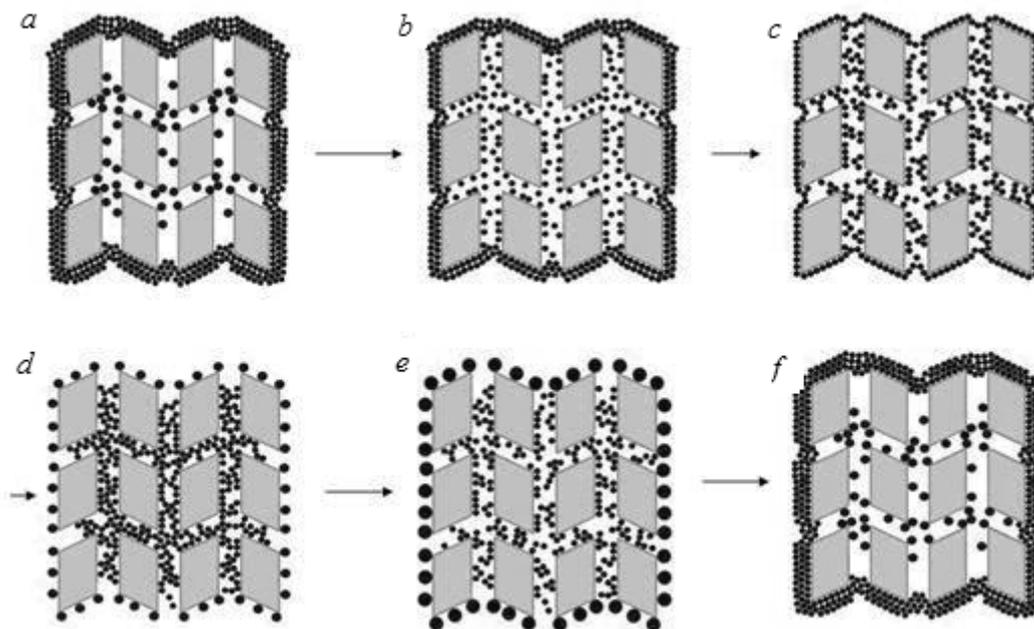


Fig. 3. Phases of continual coke motion with the vector by turns directed into the bulk of zeolite (a-c) as well as onto the external surface of zeolite crystals (d-f)

As for the switching mechanism, then it consists in the by turns now fully, now particularly occupation of the external surface with the coke when jumpy changing simultaneously the corresponding chemical

inner porous coke keeps the chemical potential value close to μ_b . And so decreasing μ_b value of the external surface coke in jumpy manner to μ_c value will cause the reverse process: expiring the inner porous coke onto external surface (Fig. 3, d). During such expiration the external surface clusters will increase in size. Increase process will occur up to moment of their fusion (Fig. 3, e) with the repeated formation of three molecular layer (Fig. 3, f) and with the jumpy increasing the external coke chemical potential to μ_b value, i.e. with the system return to the primary state (Fig. 3, a) and with the following reverse process starting: spillover of the external surface coke within the zeolite pores and so on. It is difficult to say something about the possible duration of such oscillations. Thermodynamics permits theoretically their endlessness since the system as isothermal one is supplied with the required energy continually. Thus, $\Delta\mu$ as a finite quantity (inequality 2) is driving force of both direct and reverse processes.

potentials by the above finite quantity $\Delta\mu$. Therefore, the driving force of oscillatory dynamics of coke deposits is the higher chemical potential of massive coke as compared to the chemical potential of cluster coke, and the

switching mechanism takes place due to the alternating changes of the occupation of the external surface from full to partial coverage by the coke and vice versa.

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Рухливі сили почергової динаміки коксу в дезактивованому цеоліті

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Здійснено спробу розглянути явища коливальної динаміки в цеолітах на основі участі в прямому та зворотному процесах кластерних утворень зі специфічними термодинамічними характеристиками. Останні визначаються тим, що у високотемпературній області будь-яка масивна речовина переважає ту ж речовину у вигляді кластерів за значенням хімічного потенціалу на величину $\Delta\mu$, породжуючи динамічні явища в цеолітних системах в результаті почергового злиття кластерів в масивну фазу, розпаду останньої до кластерного стану, повторного злиття кластерів і т. д. Величина $\Delta\mu$ є рушійною силою як прямого, так і зворотного процесів.

Движущие силы поочередной динамики кокса в дезактивированном цеолите

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Предпринята попытка рассмотрения явлений колебательной динамики в цеолитах на основе участия в прямом и обратном процессах кластерных образований со специфическими термодинамическими характеристиками. Последние определяются тем, что в высокотемпературной области любое массивное вещество превосходит то же вещество в виде кластеров по значению химического потенциала на величину $\Delta\mu$, порождая динамические явления в цеолитных системах в результате поочередного слияния кластеров в массивную фазу, распада последней до кластерного состояния, повторного слияния кластеров и т. д. Величина $\Delta\mu$ является движущей силой как прямого, так и обратного процессов.