A STUDY OF SURFACE MORPHOLOGY OF ZEOLITE (MAZIT) BY ATOMIC FORCE MICROSCOPY

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The surface morphology of zeolite (mazit) is investigated by atomic force microscopy under normal conditions. Application of "MD mode" regime has allowed receiving clear, with the high resolution, the image of topography high-abrasive surfaces with a high-developed of a relief. The analysis of surface structure in the "MD mode" regime has shown, that compaction the sample mazit, first, reduces range of the sizes surface crystallites, and, second, leads to formation of the big number of the small grains grouped near to borders of various breaks.

1. Introduction

Interest to nanocrystallite ceramic materials (zeolites, ceramics on the basis of various oxides) is connected with an opportunity of their practical application, for example, as high-choused catalysts of chemical reactions, absorbers of gas and etc. [1]. Zeolites (both natural and artificial) possess strongly pronounced ion-exchange and adsorptive properties, and also have rigidly sustained sizes of inputs of pores and channels (which sizes are from 0,3 up to 1,5 nm). All this allows considering them as perspective molecular filters and selective sorbets. From this point of view, the knowledge of properties and structures of the zeolites is one of ways of perfection of technological methods of their reception (first of all, compaction and sintering) [2]. The atomic force microscopy (AFM) is for today one of the basic methods of research of structural features of a surface of various types of zeolites [3].

However, at researches on air it was not possible to realize the high spatial resolution inherent in method AFM. The matter is that surfaces of zeolites are, on the one hand, high-abrasive, and with another – differ a high degree of development of a relief. Therefore, standard regimes AFM "tapping mode" and "non-contact mode" allowing investigating similar surfaces with greater difference of heights, under atmospheric conditions do not provide the sufficient resolution that is connected with presence on a surface of zeolite of the adsorbated layer [4]. Other standard regime AFM "contact mode" possesses the greatest resolution. But in this regime scanning results or in catching the probe because of a high degree of development of a relief, or to abrasion of a probe about high-abrasive a surface of zeolite [5].

In the given work the problem of reception of the image of morphology of a surface of zeolite (mazit) by method of AFM was solved under atmospheric ambience before and after compaction. For this purpose new regime AFM "MD mode" has been used (i.e. "Multi Date mode"), allowing to receive topography of a surface with the high resolution. Thus, unlike standard regimes AFM ("contact mode", "tapping mode", "non-contact mode"), it is completely excluded both abrasion of the probe, and catching of the probe at scanning a surface of the sample.

2. Force curve and AFM "MD mode" regime

As is known, the basic information signal at scanning a surface in AFM is the signal of a deviation cantilever on a normal to a surface (to a plane of scanning), and also a signal of a deviation cantilever in a plane parallel to a plane of scanning [6]. Let's remind, that registration of a signal during an approach of a probe to a surface and removal from it gives power curve S (Z), i.e. is considered a curve of dependence of size of a bend cantilever, S, from position of surface Z (if a moved element – the surface) which is set and always certain. This part of algorithm is the general for all regimes AFM. The main feature of a regime "MD mode" [7] is that the trajectory of movement of a probe at an approach-removal here essentially differs from trajectories of movement of a probe at standard regimes AFM. At an approach, the probe passes of the adsorbated layers, concerns a "pure" surface and measures its coordinates. Measurement of coordinates of topography of a surface is made in rigid contact of a probe to the sample. As the measurements are performed in full contact with the surface, resolution of “MD mode” is comparable with “contact mode” resolution. Thus, the trajectory of moving of a probe does not suppose lateral moving of a probe concerning a surface in contact that excludes abrasion or destruction of the probe. Then the probe is allocated from a surface on distance at which there is no interaction with the sample and only after that is made lateral moving to a following point of measurement. It excludes catching the probe during scanning and also lateral moving of the adsorbed layers on the surface.

Besides the probe, passing the adsorbed layers, can separately measure and their characteristics. And it means, that the regime "MD mode" allows to divide the information on a surface and the adsorbed layers on it and to receive separately both topography of a "pure" surface, and a card of distribution of thickness of the adsorbated layer on a surface [8]. Last in a regime "MD mode" turns out as follows. The probe at an approach all over again does "jump" to surface of the adsorbed layer, and after movement inside of it does one more "jump" already to a "pure" surface. Thus the coordinate of a point of a contact by a probe of a surface the adsorbated layer and coordinate of a point of a contact a probe of a "pure" surface is registered. The difference between these coordinates as a result gives thickness of the adsorbated layer in the given point of a surface. As a result, passing down-up, the probe measures characteristics the adsorbated layer and characteristics of a surface measures in contact to it already under the adsorbated layer. Therefore, first, it is possible to consider a surface "pure", and, second, influence of the adsorbated layer on the measured coordinate of a surface automatically is excluded.

3. Experimental results and discussion

High-abrasive surfaces mazit were tested by AFM "contact mode" and "MD mode" for comparison. The sample represented a powder consisting of grains of the spherical form, put on a graphite substrate. As grains under action of surface forces stick to a probe and remain on it the powder has been preliminary pressed under mechanical press

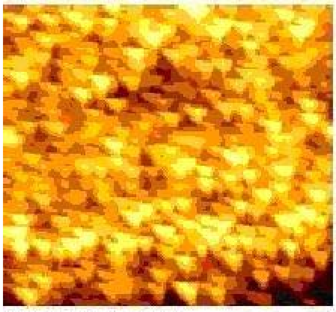

Fig. 1(a). Topographic image of a surface of mazit ("contact mode").

(diameter of pressing ~ $2{,}5\times10^{-2}$ m). After that, the pressed washer has been investigated on AFM. First, the sample of mazit has been investigated on AFM in a regime "contact mode ". In experiment the pyramid-like probe from Si_3N_4 (coefficient of elasticity cantilever 0,3 N/m was used; radius of the probe of ~120 nm and taper angle of the probe ~ 55°). At scanning a surface in a regime "contact mode" the probe or cached, or still moved on a surface of the sample and abrasives about it as about an emery paper. And the topography of a surface in this case displayed artifact "relief". In Fig. 1 (a) the topography of a surface mazit with the area of scanning 1542×1542 nm received in a regime "contact mode" is shown. On all area of the images certain isosceles triangles with the sizes of the sides 70×70×50 nm are observed. In this case we see not a surface, and of the pyramidal probe which has been abrasive about high-abrasive of surface mazit. The matter is that the image of data about a surface, strictly speaking, represents mathematical convolution of geometrical forms of a probe and a surface [9]. Therefore, when the probe,

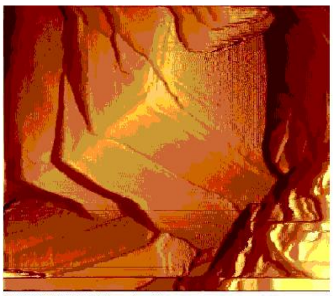

Fig. 1(b). Topographic image of a surface of mazit before compaction ("MD mode").

gradually abrasion about a surface, became more, than surface objects on the image the form of the probe was clearly visualized, instead of a surface. For check of this fact, the probe has been separately investigated on a scanning electronic microscope. Photos of the probe, made before to the beginning of experiment and right after the end of experiment, have shown that the probe has been abrasive as a result of contact to a surface. Predictably, because of high-abrasive and strongly developed surface to receive topography of the surface of mazit in a regime "contact mode" it was not possible.

In the second experiment the surface of the same sample mazit has been investigated in a mode "MD mode". During all experiment the same probe of the conic form from W (coefficient of elasticity cantilever ~ 0,3 N/m was used; radius of the probe ~ 15 nm; and taper angle of the probe ~ 27°). In Fig. 1 (b) the topography of a surface mazit with the area of scanning 1542×1542 nm received in a regime "MD mode" is shown. The image of a surface rather clear, with the high resolution (to more light tone there correspond higher point of a relief of a surface). The surface differs strongly developed relief – on the area 1542×1542 nm the range on Z from the lowest up to the highest point of a surface reaches 1001,3 nm. Here the typical microstructure of a surface mazit is observed, in particular, steps of growth crystallites are well visible. Large crystallites have the complex form with rather sharp "broken off" edges, and finer – kvazi-spherical the form. Then, with the purpose of reception of structure of higher density, the same sample mazit has been subjected to process compaction. Last was spent by means of mechanical

Fig. 1(c). Topographic image of a surface of mazit after compaction ("MD mode").

pressing (diameter of pressing $2{,}5\times10^{-2}$ m; specific pressure ~ $4{,}8\times10^{6}$ kg/m^2). In Fig. 1 (c) the surface mazit with the area of scanning 1542×1542 nm after the mechanical pressing, also received in a regime "MD mode" is shown. Here too, as well as in Fig. 1 (b), the image of a surface is observed clear, with the high resolution. After compaction, the disorder of the sizes surface crystallites, naturally, became noticeably less, i.e. the relative density of structure has increased. Thus, the average sizes of a greater part surface crystallites are within the limits ~ (200-400) nm. On a surface a plenty of small grains in the size of 16 nm $<d<$32 nm which, basically, are grouped near to borders of various breaks is observed. Apparently, mechanical compaction, influencing the sample, most actively influences structure near to internal borders crystallites , as leads to formation already nanostructure crystallites.

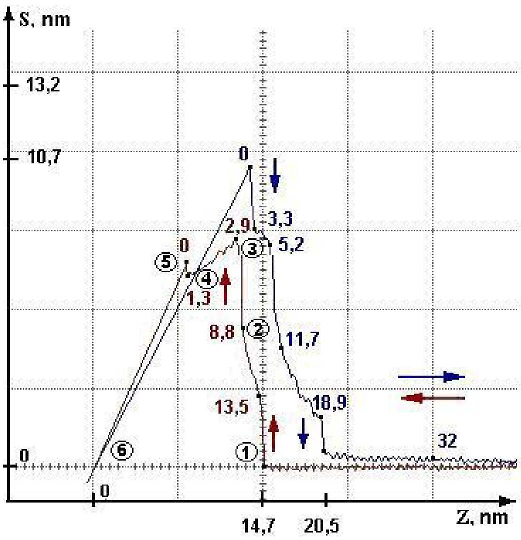

Fig. 2. Experimental force curve removed in the certain point of a surface mazit in "MD mode" regime.

In Fig. 1 (b) and in Fig. 1 (c) the clear image of a surface was observed. As the clear image obtained by the same probe is observed, it proves, indirectly, that "MD mode" is free from abrasion and catching of the probe. Both show topography of a surface the high resolution of a regime "MD mode" under normal conditions on not conductivity surface with strongly developed relief. Thus, greater advantage of a regime "MD mode" is that presence of the adsorbated layer on surfaces does not influence in no way quality of the received image of a surface. On the contrary, in addition to it, the regime "MD mode" allows to receive simultaneously and a card of distribution of thickness of the adsorbed layer on the given area of a surface [10].

Though in the given experiment such problem was not put, as an example we shall show, how the typical experimental force curve (Fig. 2), removed in the certain point of a surface mazit in a regime "MD mode" looks (arrows force curves of an approach-removal of a probe are shown). Here we shall briefly analyze only a force curve of an approach of a probe to a surface (more detail process of registration of a force curve has been considered in [11]). On a direct horizontal part the force curve probe does not cooperate neither with of the adsorbated layer, nor with a surface. In a point 1 under influence of Van-der-Waals interaction between a probe on the one hand, and a surface of the sample with of the adsorbated layer on the other hand, the probe does "jump" aside surfaces (a vertical part from a point 1 up to a point 2) and is braked by a surface of the adsorbed layer in a point 3. On a force curve it is possible to measure, that the probe passes before registered contact to a surface of the adsorbed layer in a point of 3 distance in 11,8 nm. Further, having reached a surface of the adsorbed layer, the probe presses with accruing force, is elastic deforming it on distance of 1,6 nm (a flat part from a point 3 up to a point 4; the basis cantilever thus moves on distance of 8,5 nm). Small vertical part following it from a point 4 up to a point 5 on distance of 1,3 nm it is possible to interpret as break of the adsorbed layer by a probe and consequent "jump" of a probe to a surface mazit (a point 5). Further there is the part of direct contact of the probe with a surface (from a point 5 to a point 6) on which in a point of crossing of zero (the point 6) cantilever is straightened (a point of contact balance). For an estimation of distance from of the probe to a surface in the given point, neglecting passage of a probe on curve Van-der-Waals of forces on the part between points C and D (Fig. 3a) also we shall consider, that the probe after "jump" to a surface at once reaches it and is based upon it (Fig. 3b).

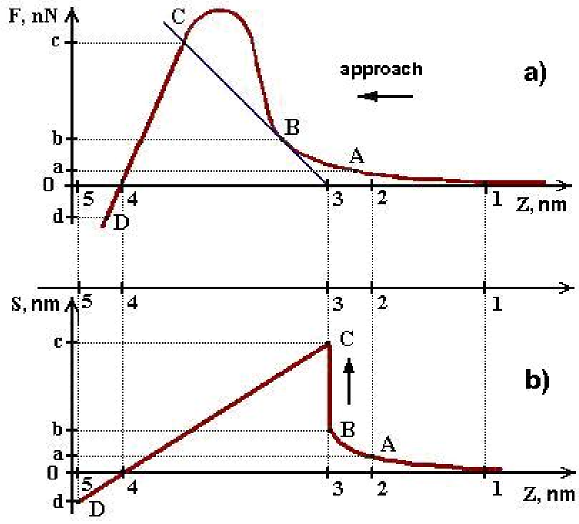

Fig. 3. The process of probe approach to the surface: Van-der-Waals interactions on the distance up F(Z) surface (a); force curve S(Z) there has been shown cantilever positions with the probe on the coordinate of surface position (b).

Obviously, that in most cases so it and occurs owing to forces of inertia and the forces of an attraction acting on a probe. So, if to consider, that in a point 5 probe gets on a surface the distance which has been passed at it by the basis cantilever, makes 14,7 nm, as is registered AFM as thickness of the adsorbated layer in the given point of a surface.

4. Conclusions

So, experiment has shown that research under atmospheric conditions of a surface mazit by means of standard regime AFM "contact mode" does not give an opportunity to receive the clear image of topography of the surface. "MD mode" regime scanning has turned out to be much more effective in this sense. It has been shown, that mechanical compaction mazit with specific pressure $4{,}8\times10^6$ kg/m^2 leads to formation of the big number of small grains which, basically, are grouped near to borders of various breaks. Thus, the given regime "MD mode" allows receive under atmospheric conditions with the high resolution the image of topography of a surface of any samples differing high-abrasive and a high degree of development of a relief. Thus presence on such surface of the adsorbated layer does not influence in no way image of a surface. The author thanks employees of laboratory probe microscopy of Technology research and development Institute (Moscow) for the given opportunity of work on AFM and valuable consultations.

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ATOM-QÜVVƏ MİKROSKOPİYASININ KÖMƏYİ İLƏ SEOLİT (MAZİT) SƏTHİN MORFOLOGİYASININ TƏDQİQİ

Atom-qüvvə mikroskopiyasının köməyi ilə seolit (mazit) səthin tədqiqi normal şəraitdə edilmişdir. “MD mode” rejimin tədbiq etməsi, yüksək abraziv və relyefi yüksək dərəcədə inkişaf olan səthin topografiyasının şəklini aydın və böyük böyüdülmə ilə alınmasına imkan verdi. “MD mode” rejimi ilə səthin strukturasının analizi göstərdi ki, mazit nümunəsinin preslənməsi, birincisi, səthin kristallitlərinin ölçüsünü azaldır, ikincisi, cürbəcür sındırmaların həddlərin yanında toplaşan böyük saylı xırda dənələrin əmələ gəlməyinə səbəb olur.

С.Д. Алекперов

ИССЛЕДОВАНИЕ МОРФОЛОГИИ ПОВЕРХНОСТИ ЦЕОЛИТА (МАЗИТА) С ПОМОЩЬЮ АТОМНО-СИЛОВОЙ МИКРОСКОПИИ

С помощью атомно-силового микроскопии исследована поверхность цеолита (мазита) при нормальных условиях. Применение режима “MD mode” позволило получить четкое, с высоким разрешением, изображение топографии высокоабразивной поверхности, с высокой степенью развитости рельефа. Анализ структуры поверхности в режиме “MD mode” показал, что компактирование образца мазита, во-первых, уменьшает разброс размеров поверхностных кристаллитов, а во-вторых, приводит к образованию большого числа мелких зерен, группирующихся вблизи границ различных разломов.

Received: 14.04.08