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Article

A New Method for Characterization of Natural Zeolites and Organic Nanostructure using Atomic Force Microscopy

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Abstract: In order to study and develop an economic solution to environmental pollution in water a wide variety of material were investigated. Natural zeolites emerge from that research as the best in class of this category. Zeolites are natural materials relatively abundant and non biodegradable, economic and good to perform processes of environmental remediation. This paper contains a full description of a new method to characterize superficial properties of natural zeolites of exotic provenience (Caribbean Islets) with atomic force microscopy (AFM). AFM works with the optical microscope simplicity and the high resolution typical of a transmission electron microscope (TEM). Structural information of mesoporous material is obtained using scanning and transmission electron microscopy (SEM and TEM), only if the sample is conductive, otherwise the sample has to be processed through the grafitation technique, but this procedure induces errors of topography. Therefore, the existing AFM method, to observe zeolite powders, is made in a liquid cell-head scanner, but this work puts in evidence and confirms that it is possible to use an ambient air-head scanner to obtain a new kind of microtopography. Once optimized, this new method allows investigating of organic micelles, very soft nanostructure, of cetyltrimmonium bromide (CTAB) upon an inorganic surface such as natural zeolites. It is shown some correlation between SEM microphotographies and AFM 3D images.

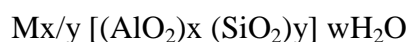
Keywords: Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), cetyltrimmonium bromide (CTAB), Zeolites, Microtopography

1. Introduction

There are several natural substances not degradable and renewable, such as zeolites [1], that are the right solution to environmental remediation, in particular some zeolites are ideal for aquifers polluted by toxic compounds such as hydrocarbons and organochlorinated [2].

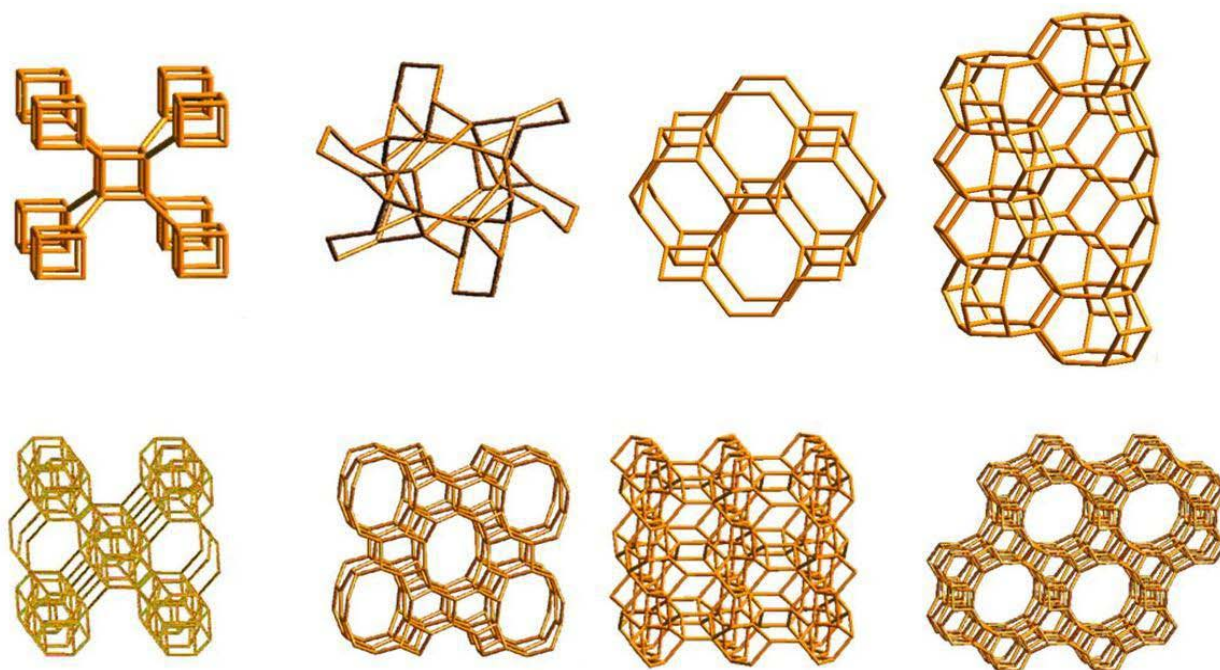
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Zeolites (Greek, zein, "to boil"; lithos, "a stone") are hydrated aluminosilicate minerals and have a micro-porous structure. The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral, that the stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils," he called this material zeolite. More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known [1]. Zeolites have an "open" structure that can accommodate a wide variety of cations, such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are: analcime, chabazite, heulandite, natrolite, phillipsite, and stilbite [1]. The general formula of a zeolite is



M is the cation, w is the number of molecules of water and the ratio x/y is the dependent parameter of the structure between 1 and 5. Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallized in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential. Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves" [3,4]. The term molecular sieve refers to a particular property of these materials, i.e. the ability to selectively sort molecules based primarily on a size exclusion process (fig.1). This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8 ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure [5]. Therefore, the pore openings for all rings of one size are not identical [6,7].

Figure 1. Molecular sieves. Microporous molecular structures of some Zeolites are shown into their atomistic representations. Image modified from Atlas of Zeolites.



2. Results and Discussion

The use of surfactant (or amphiphilic molecule) is necessary to functionalize the surface of the samples in order to have a new sovramolecular structure which enables the exchange anion [8,9] referring to appropriate molecules such as ammonium salts of long chain (CTAB) [10]. The main idea is that individual chains of surfactant enter into the typical cavity of zeolite structures and others overlap the previous ones to form a classical fluid mosaic and/or micelles. The polar part, the one with the counter ion (usually a halide) is always turned outwards, this situation allows the anions can be replaced by other ions present in the environment. The above phenomenon has already been theoretically predicted and observed with fluorescence studies [10]. In the present article a new method for the characterization of inorganic surfaces functionalized amphiphilic organic molecules is discussed. It was chosen to use as the surfactant cetyltrimethylammonium bromide (CTAB), because in the literature it is already being used in work on zeolites, in reference to their curves of adsorption [11]. As expected from the packing parameters, gives rise to cylindrical micelle structure and increase in concentration in hexagonal structures [12,13]. The different sovramolecular structures depending on the concentration of the surfactant and the temperature, at high temperatures develop a *cloud point* corresponding to the temperature where the surfactant forms a precipitate amount, At this point it's not possible to identify more ordered sovramolecular structures. Before observing, of the structural

changes determined by the dispersion of surface-carried by a solvent on a tablet of zeolite, we saw reproducibility of the scanned image [14], and any mechanical effects produced on the surface by the solvent alone (a 'drop of water' on the surface that may confuse the observation). In order to verify the reproducibility of the acquisition of these particular samples, we need to determine both the possibility of repeating the scan of the same area (pointing and centering of the sample), and to assess the real spatial resolution, which is verifying the 'maximum' magnification showing the details for which reproduced.

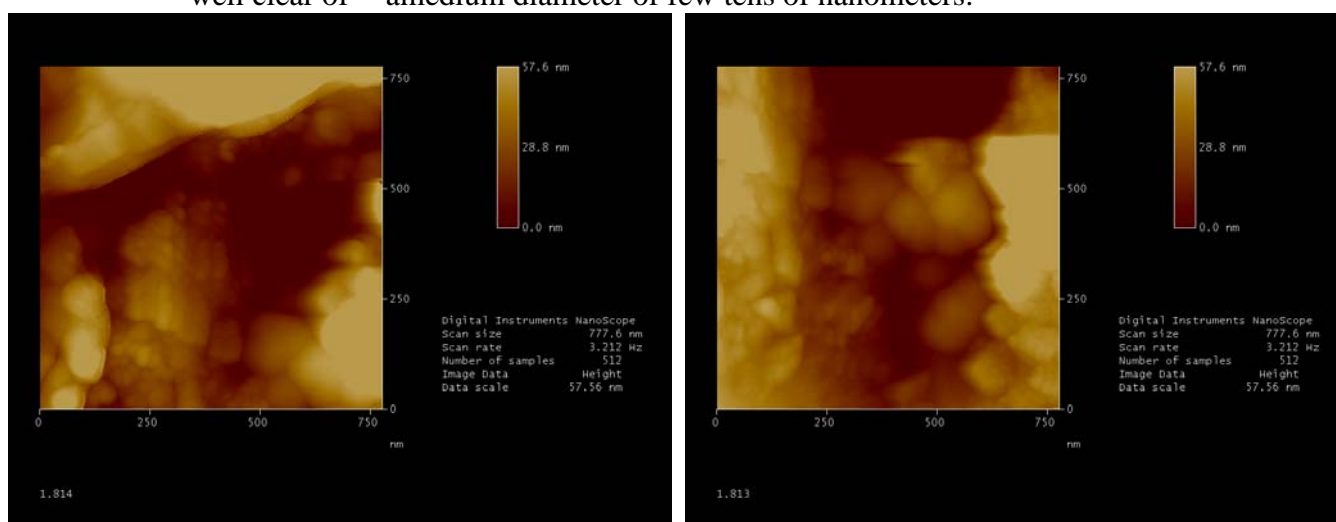
1. To allow the centering of an area of 200 nm from the side (of such size, ie, that the images have a resolution of about ten nm) procedures can 'zoom' more gradually, becoming in succession areas as large (length side) respectively equal to 10 μm , 2.5 μm , 1 μm until 200 nm. Thus it has been possible to re-scan the same area, to the nearest ten nanometers.
2. The images, obtained at different times, show that, without prejudice to possible artifacts easily identified, the details of tens of nanometers are faithfully reproduced. As this suggests, the technique used allows obtaining images with a real spatial resolution of tens of nanometers. To observe the possible effects due to interaction of the tablet with the solvent alone, a volume of 50 μL of distilled water was placed on the surface, using a microvial for gaschromatography, than left spread over the region by capillarity; Several images were acquired without solution of continuity (that shows how versatile is the technique used). It is observed (fig. 3) that when the liquid spreads on the area being scanned, capillarity forces the same solvent to hide the structure of the surface: the effect of the solvent seems to gradually cover the surface and temporarily creating a film of water molecules that prevents the acquisition of the data except at the deepest invaginations.

When the surface dries out, the overall look (scan length of 10 μm) is preserved, with clusters of spherical grains of size ranging from tens to hundreds of nanometers interspersed with areas of vacuum variable depth as well. These grains are often mixed together so that the image appears, at first view, less resolved. This phenomenon appears to be perfectly reproducible.

In fig.4.A the data has a high resolution and low background noise and shows well how the surface at a scale of 1 micron is not flat, again in fig.4.B it is possible to see the effect of solvent on the zeolite. The structures which form the morphology after adsorption of water swell. Repeating the test with a surfactant solution, you get the picture presented in fig.4.C where they show further invagination of the surface is directly proportional to the quantity of solution adsorbed. Echoing the acquisitions at different times (up to ten days) you will find the same structures, demonstrating that the modeling of

the surface is final and permanent over time. The false colors image used to highlight the heights and depths on the lighter colors correspond to the highest parts and the darker colors represent the invaginations. In fig.4.D an analysis carried out by software of the topography of a tablet of zeolites is reported. That said, if you look at the images with greater detail, we note the presence of pseudo-spherical shape with a diameter of several tens of nanometers. It is conceivable that these forms are really attributable to the surfactant micelles (fig. 2). Such presence is in fact spread over the whole area of the tablet by wet solution with surfactant.

Figure 2. AFM image obtained by “tapping mode”. Micellar structures are well clear of a medium diameter of few tens of nanometers.



Sorption: theoretical limit between ad/absorption

Sorption refers to the action of either absorption or adsorption. As such it is the effect of gases or liquids being incorporated into a material of a different state and adhering to the surface of another molecule. Absorption is the incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases being absorbed by a liquid). Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another molecule. Observing an effect of sorption on a surface at nanoscale, it becomes particularly difficult to understand the nature of the phenomenon. Under these conditions, the forces of physical and chemical nature are the same [15].

Table 1. Characteristic of zeolite investigated in this work from the island of Cuba.

Mineralogical characteristics of Zook® Zeolites				Physic properties	
Mineralogical composition (DXR): Clioptiolite 68%				Specific density: 2.10-2.24g/cm ³	
SiO ₂	64.27	K ₂ O	1.18	Volumetric density: 870-850 Kg/cm ³	
Al ₂ O ₃	13.72	CaO	4.96	Thermal stability:400 °C	
Fe ₂ O ₃	2.74	MgO	1.22	Exchange capacity for ammonium: 20 meq/100 g	
Na ₂ O	2.21	TiO ₂	0.45	Color: Green	

Figure 3. Solvent Effect. The sequence of images shows the advancing solvent front (B, C and D); the surface completely covered (E) and after evaporation (F). In G is shown the preservation of surface and its relative structures. In H is shown the picture with respective processed data during a single measure.

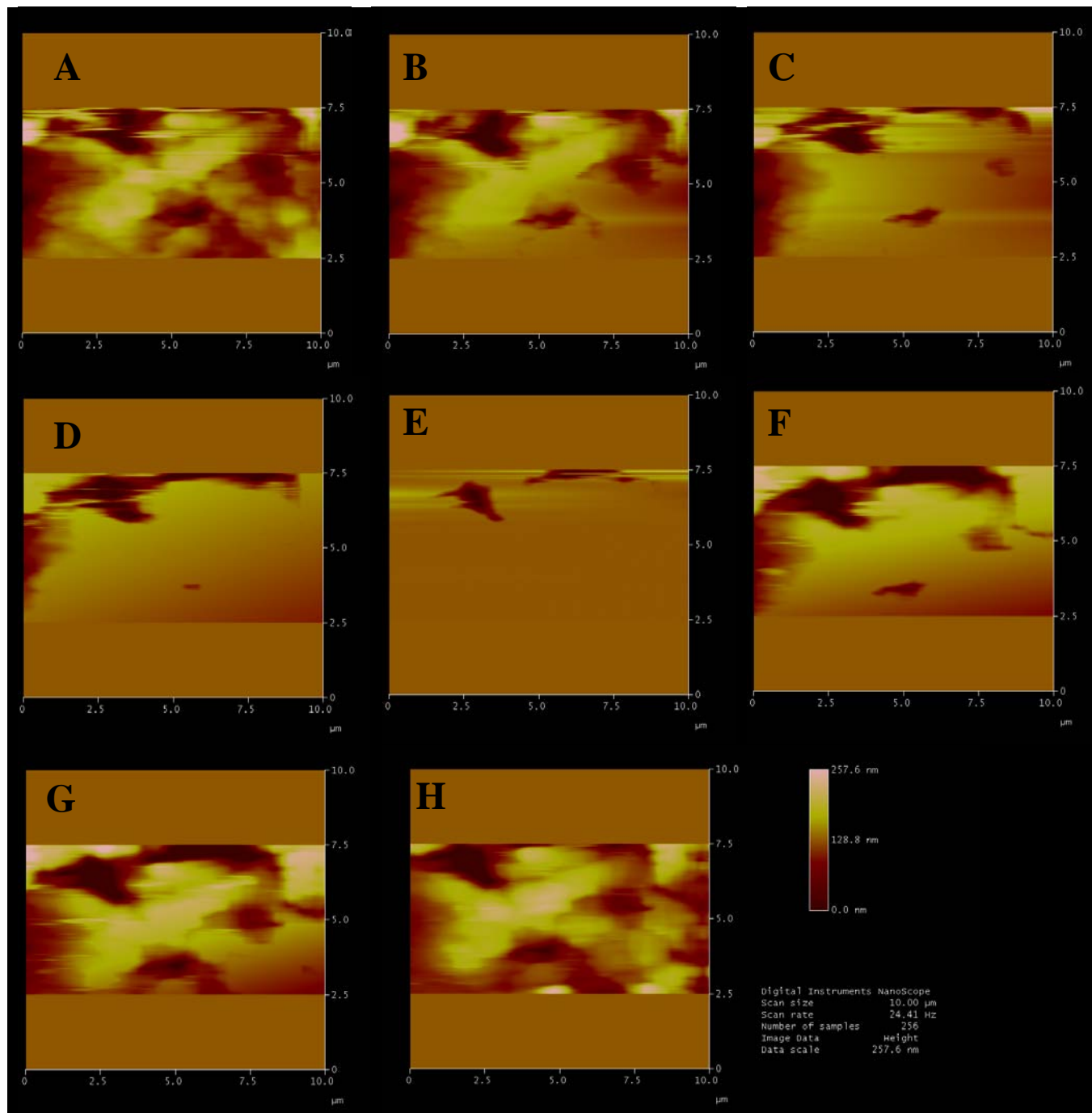
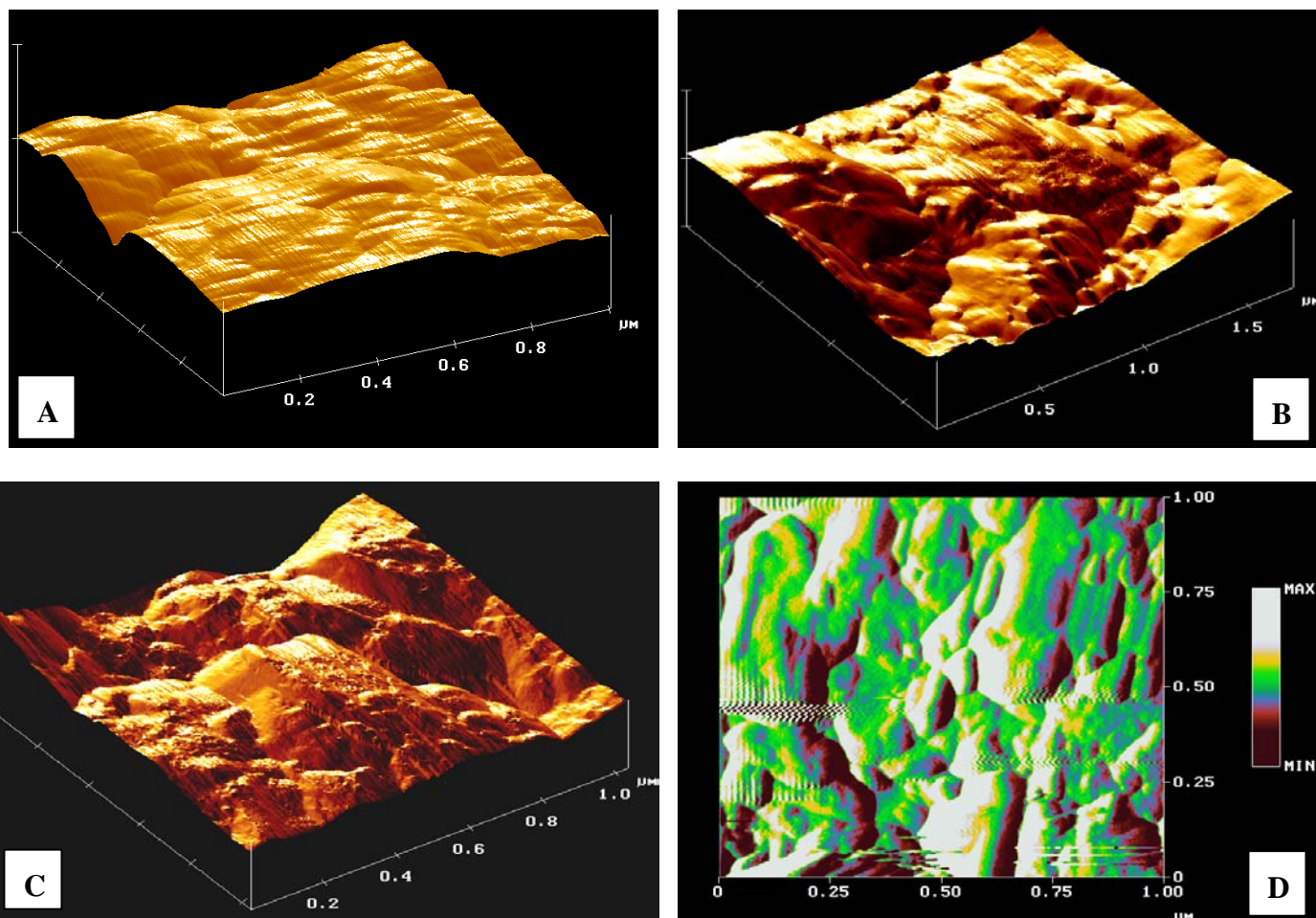


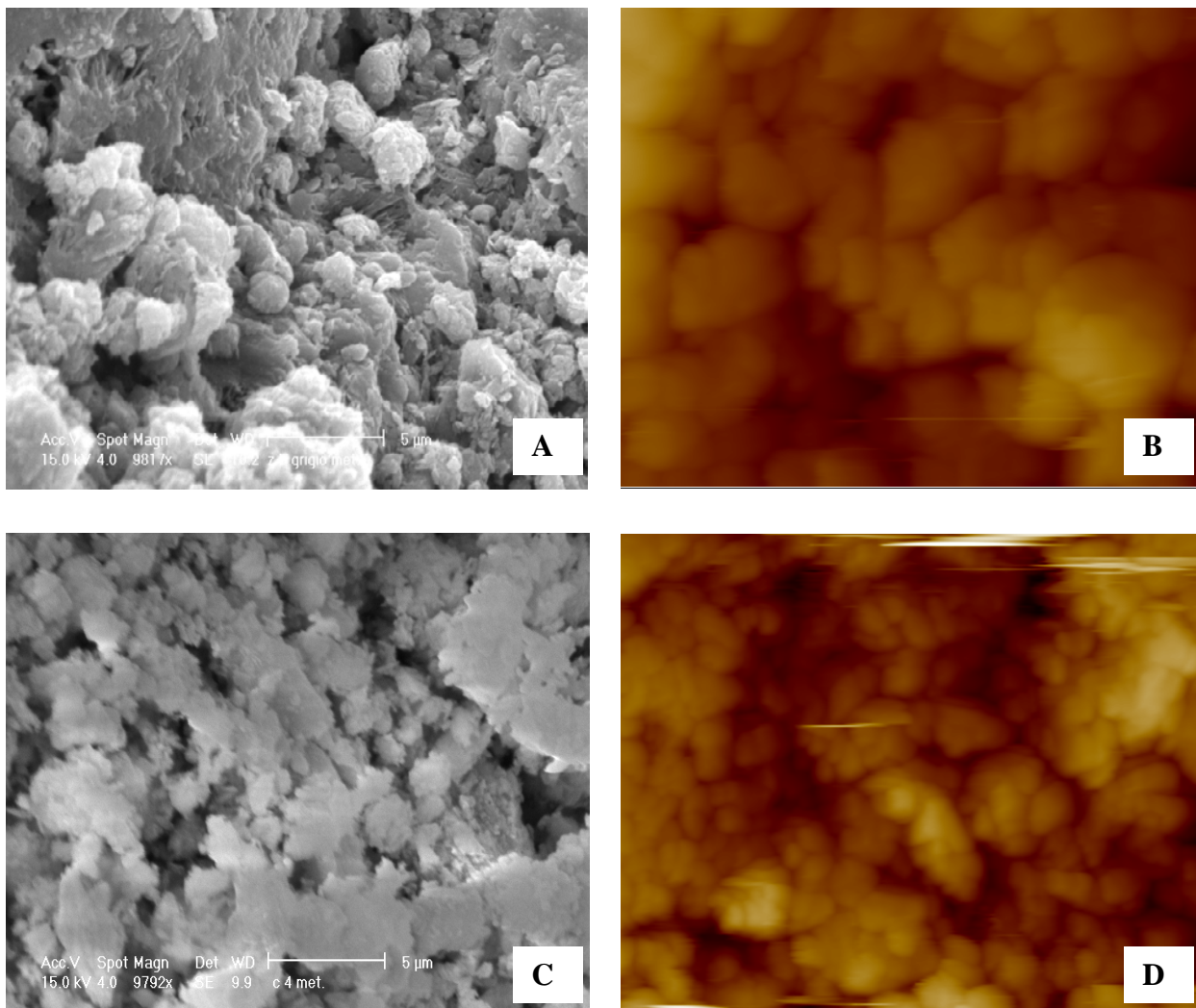
Figure 4. Three-Dimensional elaboration of scanned surface. The sample shows in the picture is a compressed of micronized powder of zeolites derivative from a Clinoptilolite mineral. A) surface at full scale of 1 μm ; B) same surface after the absorption of 150 μL of solvent; C) same surface after the absorption of 150 μL of surfactant solution; D) false color image of xy plane of same zeolite area.



2.1 Image analysis with AFM and SEM techniques.

This comparison is not intended to determine which instruments have the best image resolution. Because they are different techniques used for different purposes. It is evident from what has been said so far, that the AFM images can be helpful for understanding the SEM photomicrographs. However, an important aspect is the need to work for little conductive matrix, between the two microscopic techniques, by the “method of graphite” in the SEM observation. This practice alters the surface of mesoporous materials deeply [16-21].

Figure 5. Comparison between AFM and SEM. In A and C are shown a photomicrograph highlighting the presence of clusters of granules. In B and D, the AFM image of the same zeolites matrix powder. All the measures were carried out at the same full scale of 20 μm to better be correlated.



3. Experimental Section

3.1 Proprieties of Material

Natural zeolite studied in this work is a derivate of Clinoptilolite mineral (see mineral schedule, table1), coming from CUBA with ZOOK[®] as commercial name, take from Sereco Biotest, Perugia, Italy. Clinoptilolite is a natural zeolite comprising a microporous arrangement of silica and alumina tetrahedra. It has the complex formula: $(\text{Na,K,Ca})_2\text{-3Al}_3(\text{Al,Si})_2\text{Si}_{13}\text{O}_{36}\cdot 12(\text{H}_2\text{O})$. It forms white to reddish tabular monoclinic tectosilicate crystals with a Mohs hardness of 3.5 to 4 and a specific gravity of 2.1 to 2.2. It commonly occurs as a devitrification product of volcanic glass shards in tuff and as vesicle fillings in basalts, andesites and rhyolites. It was described in 1969 from an occurrence in Owl

Canyon, San Bernardino County, California. The use of clinoptilolite in industry and academia focuses on its ion exchange properties having a strong exchange affinity for ammonia (NH_4^+). A typical example of this is in its use as an enzyme based urea sensor. It is also used as fertiliser. Research is generally focused around the shores of the Aegean Sea due to the abundance of natural clinoptilolite in easily accessible surface deposits.

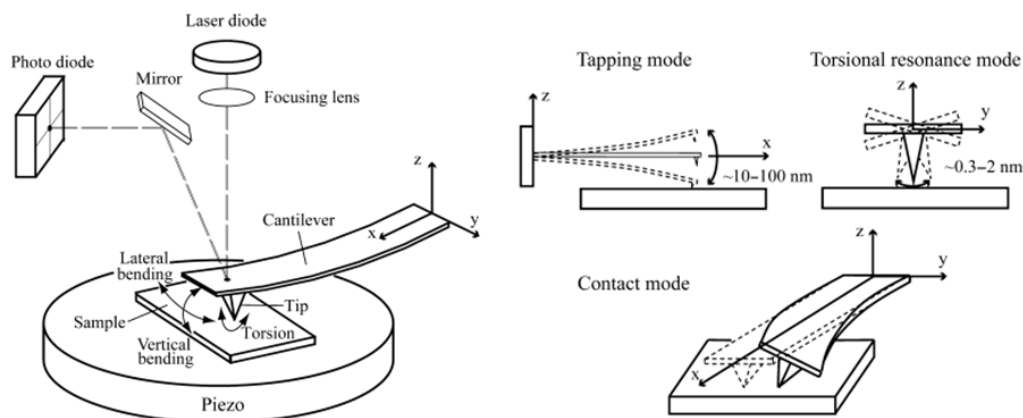
3.2 Preparation of Samples

Understanding the impossibility to study natural crystals of zeolites using AFM, we powder them with mortar and pestle and then scouring them by sieves of $40\ \mu\text{m}$ mesh. Samples with two parallel surfaces were obtained using a press for normal tablets from powder. Parameters for a good compaction are 300 mg of powder under pressure of 10 tonnes for 30 seconds under high vacuum, of course with inelastic powder.

3.3 Instruments

In several experiments, a surfactant solution was prepared by dissolving cetyltrimethyl ammonium bromide (CTAB) in water followed by 30 min of stirring to obtain the critical micellar concentration. AFM data were collected by a Digital Instruments-Veeco [22], now Bruker, MultiMode Nanoscope III (fig.6). A silicon nitride cantilever (Digital Instruments) was scanned over the zeolite surfaces in contact and tapping mode at 8 lines/s. Imaging forces were minimized and estimated to be on the order of 5 nN. SEM data were performed in the Centro di Microscopia Elettronico of University of Perugia using a model Philips XL30. The high tension output can be linearly regulated from 0.2 to 30 kV and the magnification from 10 to 400.000x. This model is endowed of a LaB6 electron source that enables a very high definition of 27 Megapixel, coupled with a Silicon Graphics imaging processor.

Figure 6. Atomic Force Microscopy. Schematic diagram of AFM and three different AFM operating mode. In this paper are used Tapping and Contact Modes



3.4 Experimental Procedure.

This work is focused on examining the changes induced on surface of tablets using solvents and surfactant solutions and their observing by Atomic Force Microscopy (AFM). The experiment is produced in four phases:

1. Scanning some areas of surface with different zoom from 10 μ m until 200nm as full scale.
2. Adding 50 μ L of distilled water (using a microvial for gaschromatography) on the region scanned.
3. After surface scanning, dried again the same region from 10 μ m until 200nm as full scale, to observe the reproducibility of phenomenon.
4. When the phases above are set up, it is possible to observe organic nanostructure such as fatty acid micelles, using CTAB.

4. Conclusions

Zeolites are a class of microporous crystalline materials that have been widely used as catalysits, adsorbents and ion-exchangers. Zeolites contain uniformly sized pores in the range of 3-10 Å and can display molecular recognition, discrimination, and organization properties with a resolution of less than 1 Å. Zeolites characteristic depend on the nature of their pore opening and their hydrophobic or hydrophilic properties.

This article is focus on two issues: the development of a new method to investigate the surface properties of the zeolites with the AFM Nanoscope III and the study of changes induced on the surface of mesoporous matrices by surfactant solutions. The method discussed here is a novel and flexible strategy to use and less expensive than others that study the microscopy of powder in solution with special AFM liquid-cell mounted in the scanner head of the instruments.

AFM confirms is reliability as an advanced microscopy technique by multi-use: working in contact mode it is observed in real time the effect of solvent on a surface of mesoporous tablets micronized zeolite; on the contrary, working in tapping mode it is observed well structured CTAB micelles. Finally, it was possible to observe the sovramolecular structures (micelles) of the surfactant and how they are arranged on the surface of the zeolite. All these images carried out are important information to current knowledge on the possibilities to use AFM for this type of samples and for the characterization of powder of micronized materials. Future prospects are wide ranging, especially in the field of functionalized nanomaterials for the environmental remediation using very economic systems.

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