

NATURAL CLINOPTILOLITE NANOPATELETS PRODUCTION BY A FRICTION-BASED TECHNOLOGY

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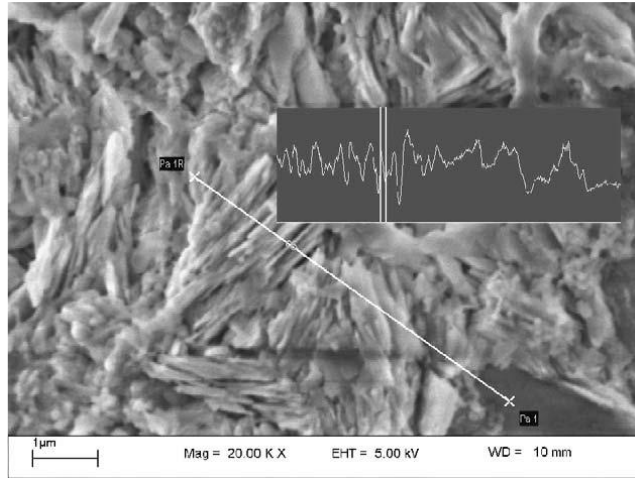
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NANOSTRUCTURED TEXTURE OF NATURAL CLINOPTILOLITE



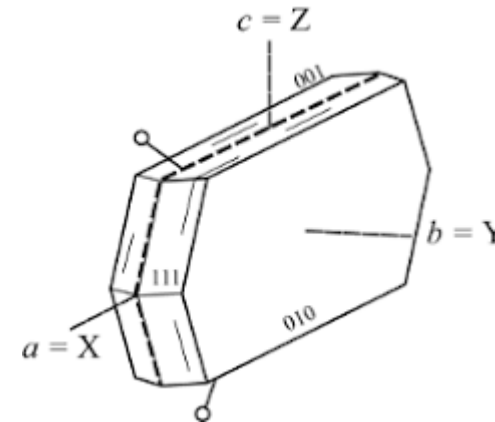
Natural clinoptilolite in granular form.



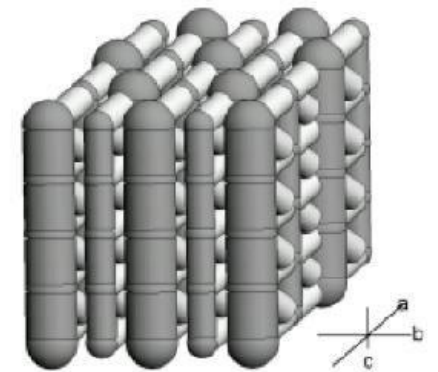
Nanostructured texture of geomorphic clinoptilolite.

The channels form a two-dimensional network parallel to the lamella basal planes (010). Consequently, the porosity of the supported lamellas is fully accessible.

Geomorphic clinoptilolite is made of single lamellar crystals very compactly stacked together. These aggregates can be mechanically exfoliated in order to achieve the single units. Since these crystals have a thickness of only 40 nm, they could be considered as 2D nanomaterials.



Clinoptilolite lamellar crystal.

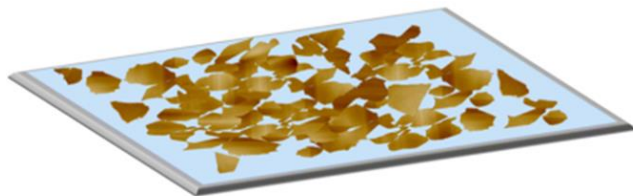


Channels orientation in the single lamellar crystals.

2D CLINOPTILOLITE NANOPATELETS AS MOLECULAR TRAPS FOR VOCs

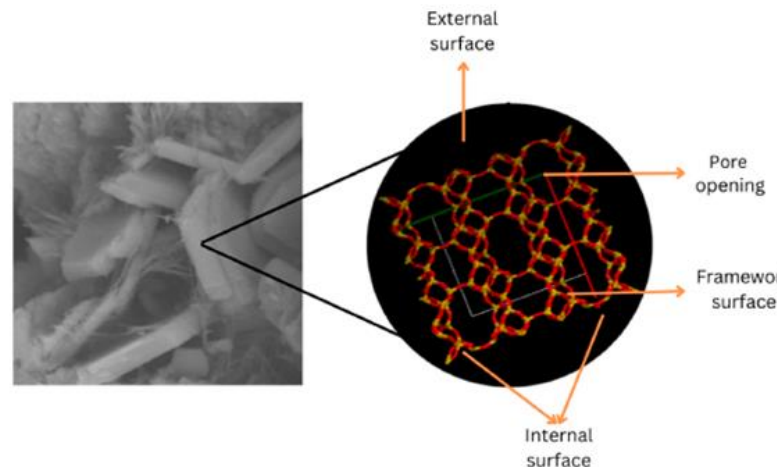
1. Clinoptilolite nanoplatelets can be technologically exploited as molecular traps for VOCs. Owing to their planar lamellar shape, these nanostructures can be easily supported on an adequate substrates (e.g., plastic films, paper sheets, etc.);
2. Since the two-dimensional system of channels, that are running parallel to (010) plane, has a length of a few hundred microns, the platelets can operate as a diffusive molecular trap;
3. The clinoptilolite porosity of a few angstroms allows a facile access to small gaseous molecules as VOCs. During the trap exposition to the contaminated environments, VOCs permeate the zeolite porosity by diffusion. However, the reverse process takes place very slowly, because of the large channel length.

1



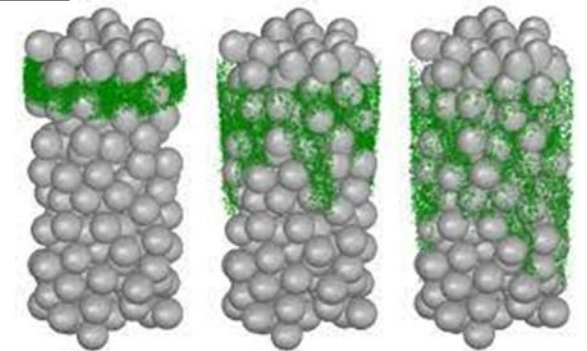
*Strong adhesion to the substrate
due to the high surface contact.*

2



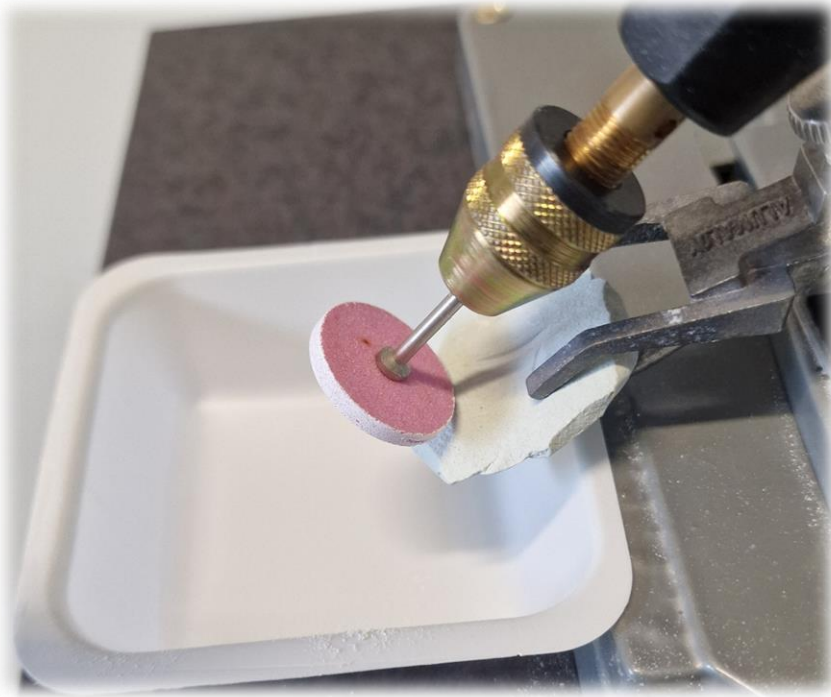
Channels oriented along the c axes.

3



*VOCs diffusion in
clinoptilolite channels.*

ABRASION DRILL TECHNOLOGY FOR NATURAL CLINOPTILOLITE NANOPLATELETS PRODUCTION

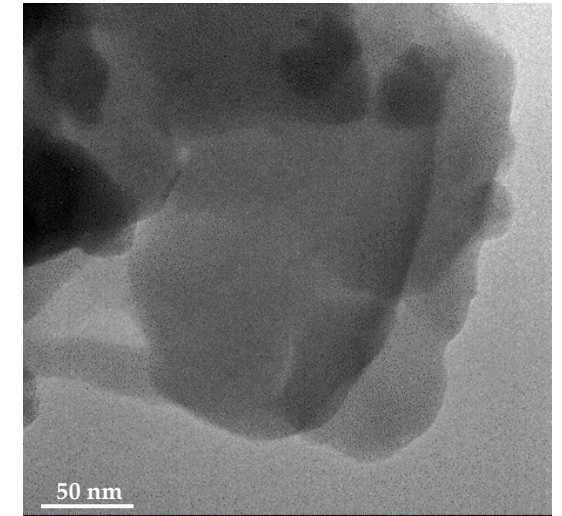
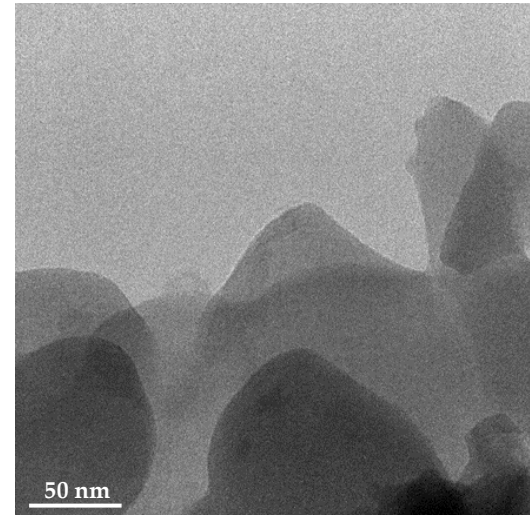
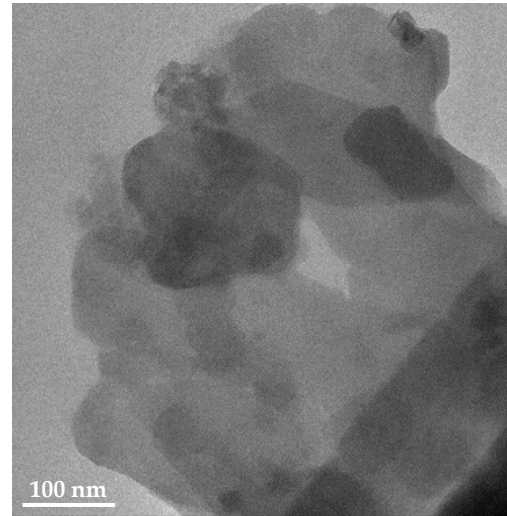
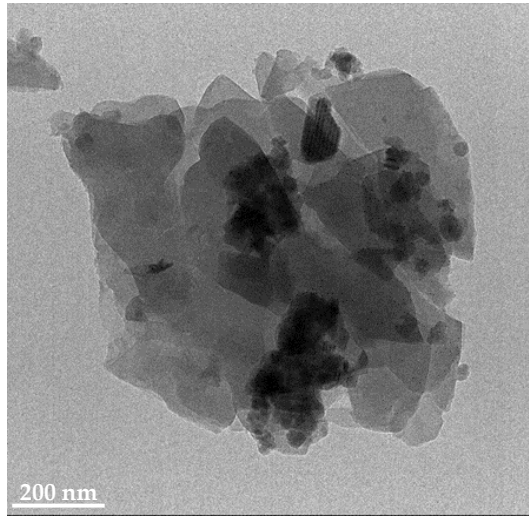


*Abrasion drill apparatus used for the
powders production.*



The abrasive drill has been put in contact with one edge of the stone in order to apply a friction force to the sample surface. The exfoliation was performed at a constant speed (ca. 3,000 rpm) and at under minimum applied load.

TEM CHARACTERIZATION OF CLINOPTILOLITE AGGREGATES



TEM micrographs of micro-aggregates of clinoptilolite produced by the abrasion-drill technology

The obtained micro-aggregates have been morphologically analyzed by TEM. Lamellas can be distinguished on the basis of their different gray-scales. These aggregates show a brittle-type fracture and the absence of defects.

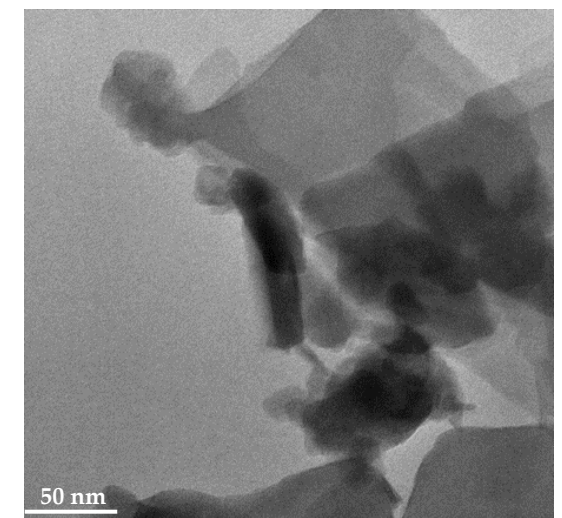
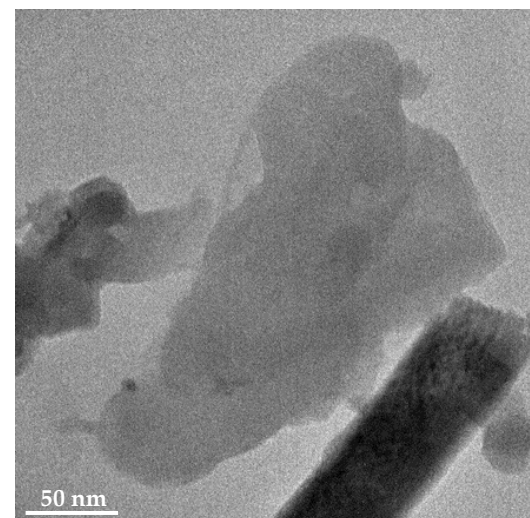
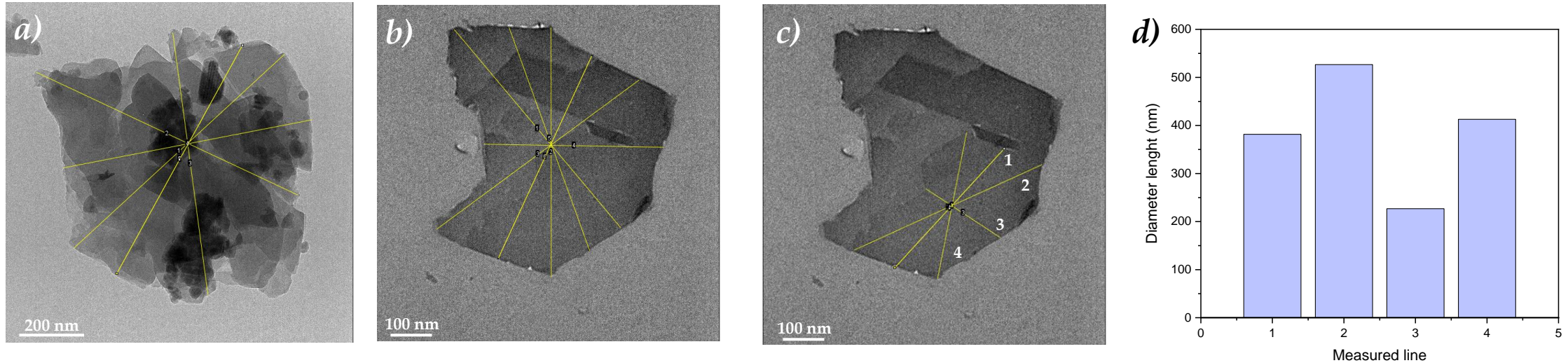


IMAGE ANALYSIS OF THE CLINOPTILOLITE LAMELLAR AGGREGATES

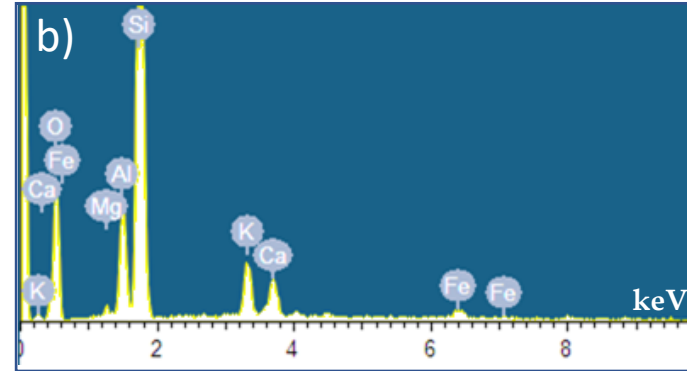
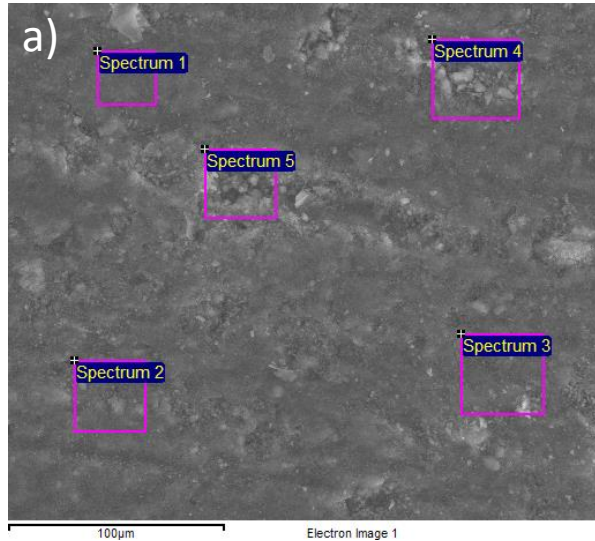


Measurement of the average diameter of clinoptilolite lamellar aggregates.

Size measurements of one of the lamellas contained in the aggregate.

The analysis of the average sizes of micro-aggregates (a, b) and single lamellar crystals (c) of clinoptilolite are performed by using the “ImageJ” Software analysis. Owing to these analysis it is possible to determine the average sizes of both micro-aggregates and single lamellar crystals (d), that is varying from 200 to 500 nm.

EDS CHARACTERIZATION OF THE CLINOPTILOLITE AGGREGATES

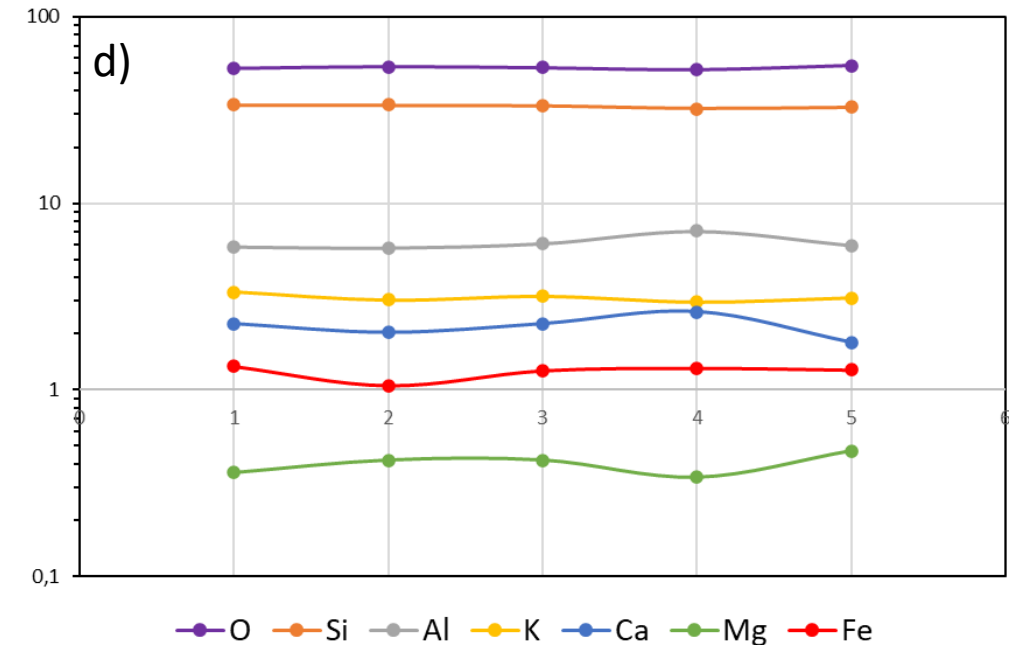


C) Atomic percentages of the elements present in the sample

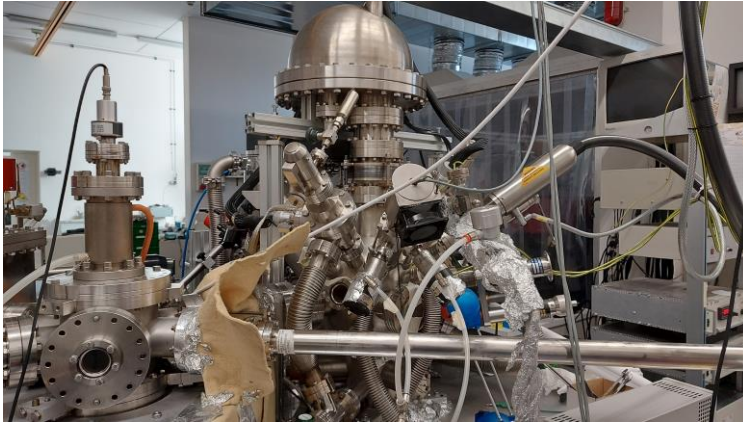
Areas	O	Si	Al	K	Ca	Mg	Fe
1	53,1	33,8	5,8	3,3	2,3	0,4	1,3
2	54,1	33,7	5,7	3,0	2,0	0,4	1,1
3	53,4	33,4	6,1	3,2	2,3	0,4	1,3
4	52,4	32,1	7,1	3,0	2,6	0,3	1,3
5	54,8	32,7	5,9	3,1	1,8	0,5	1,3

Analysed areas (a), EDS-spectrum (b), sample elemental composition in the analysed areas (c) and compositional homogeneity obtained by EDS analyses (d) of the clinoptilolite sample.

According to the EDS analysis, the sample consisted of the clinoptilolite–K,Ca. In addition, little variations in the sample composition have been found only for cations present at low concentration.



XPS SURFACE CHARACTERIZATION OF THE AGGREGATES



UHV Chamber equipped with

VSW HA100 analyser

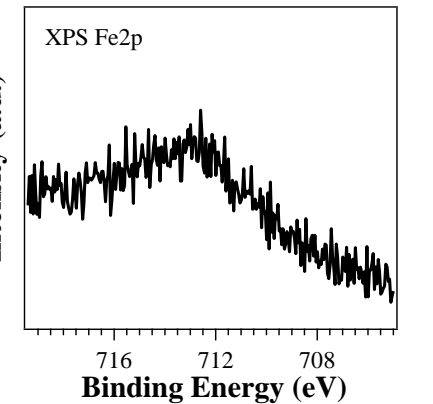
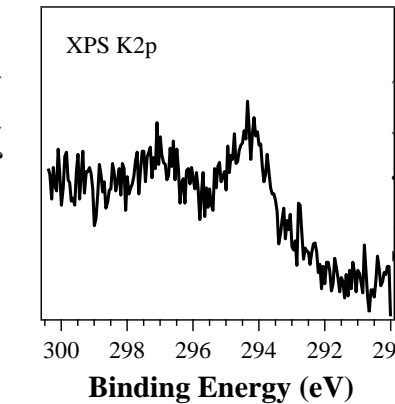
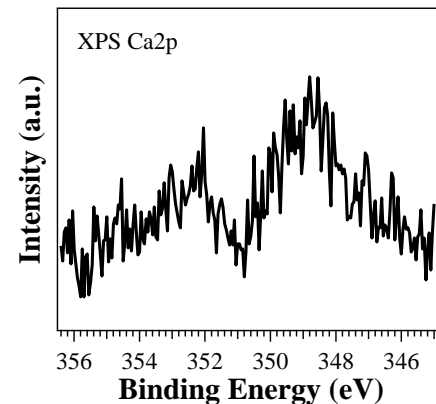
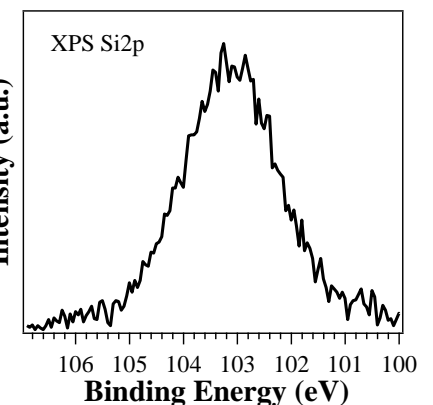
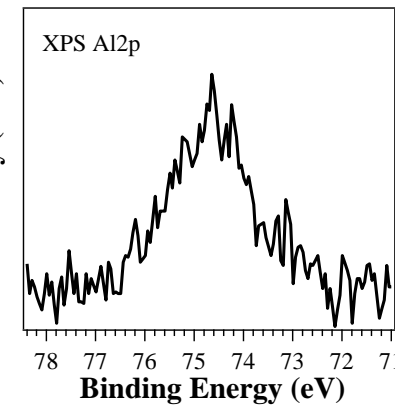
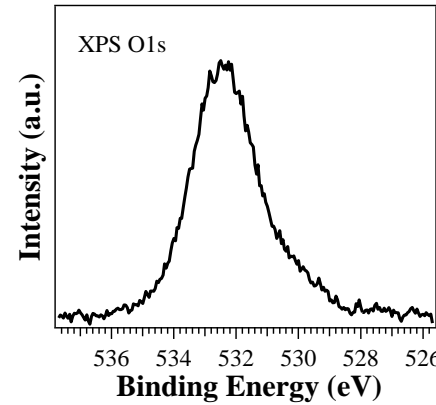
XPS): X-Ray source VG 8600 dual anode @ 1253.6eV ($MgK\alpha$)

UPS: UV lamp, HeI (21.22eV) and HeII (40.8 eV)

AES: e-beam LEG62 ThermoVG @ 3-5 KeV spot size down to 5 μ m

LEED: LaB₆ filament, reverse view, energy range 10-1000 eV

Ion Gun VG EX03: Ar+, 0.3 to 3 KeV



XPS spectra @ PE=20eV of all chemical species on the surface, for quantitative analysis of Clinoptilolite in powder form (supported on carbon tape)

CONCLUSIONS

- I. Natural clinoptilolite has a nanostructured texture, that is made of 40 nm thick single lamellar crystals stacked together;
- II. The clinoptilolite structure can be exfoliated by applying a friction force to the sample surface;
- III. The number of the lamellas per aggregate and the average size of the both aggregates and single lamellar crystals can be easily obtained by the morphological analysis (TEM);
- IV. Zeolite type identification and the homogeneity of the elemental composition has been determined by EDS analysis;
- V. Clinoptilolite nanoplatelets can be conveniently obtain by using the abrasion-drill technology;
- VI. The obtained nanoplatelets have a convenient shape to be used in a supported form as required to fabricate molecular traps for VOCs.