

Natural Clinoptilolite Nanoplatelets Production by a Friction-Based Technology †

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Abstract: Molecular traps, based on natural zeolites, are being used to remove harmful gaseous substances (VOCs). These chemical devices must be supported on an adequate substrate (e.g., paper, polymeric films, etc.). To achieve very strong adhesion with the substrate, the planar shape is the most convenient choice for these systems. Clinoptilolite is a nanostructured material made of nanosized lamellae with a thickness of 40 nm. A new technological approach, based on the use of an abrasive drill, was selected to exfoliate a natural clinoptilolite sample, thus leading to a powder made of single lamellar crystals. The obtained lamellae have been characterized by TEM, SEM/EDS, and XPS.

Keywords: clinoptilolite; nanoplatelets; lamella; molecular traps; VOCs; abrasion drill

1. Introduction

Porous ceramic nanostructures have several technologically useful physical/chemical properties that can be provided to a substrate to achieve a functional material. Zeolites have interesting adsorption properties [1–4], related to the ordered porosity that characterizes their crystalline lattice. Indeed, a regular array of nanoscopic channels, crossing the full bulk structure of this silico-aluminate compound, can store a large amount of very small polar molecules (e.g., CO₂, CH₂O, CO, NH₃, etc.). Such molecules interact with the extra-framework cations through strong ion–dipole bonds (ca. 80 kcal/mol) [5]. A possible industrial application of the zeolite adsorption capability is represented by the molecular traps [6–8], which are special chemical devices able to remove harmful gaseous substances (i.e., VOCs) from the environment by a physical/chemical adsorption mechanism. The use of nano-sized zeolites as air pollutant adsorbents offers the great advantage of faster adsorption kinetics due to the wide external surface area typical of a nanometric powder. Many nature-made zeolites have a nanostructured texture [9,10] that can lead to nanopowders if a convenient disaggregation technique is applied. In particular, natural clinoptilolite is made of randomly-oriented stacks of nanoplatelets with a thickness of 40 nm and the other two sizes of a few hundred microns [11]. It is possible to cleave up the nano-platelets from the nanostructured mineral by using an opportunely selected disaggregation treatment. To detach the nanoplatelets from each other, the application of a tangential force (i.e., a shear stress) is required. Such force can be conveniently generated by friction acting at the surface of the raw mineral grains without applying significant compression. Due to their planar shape, nanoplatelets can be firmly supported on a cellulose or polymeric substrate since the large contact surface area allows for very good adhesion characteristics. Recently, molecular traps based on powdered zeolite have been used to functionalize printed paper



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to solve the indoor pollution problem [12]. In this case, the ink used for the printing can guarantee the required adhesion characteristics.

Here, a simple technology based on an abrasion drill has been adopted to obtain single platelets of clinoptilolite starting from a natural clinoptilolite sample. The obtained nanopowders have been morphologically characterized by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM/EDS). In addition, the chemical composition of these nanopowders has been investigated by X-ray photoelectron spectroscopy (XPS).

2. Materials and Methods

The exfoliation experiments were performed on mineral clinoptilolite provided by TIP (Technische Industrie Produkte, GmbH, Waibstadt, Germany). The raw material is made of polydisperse grains with sizes ranging from a few millimeters to a few centimeters. A stone having a diameter of ca. 5 cm was selected for the nanoplatelet cleavage treatments. In particular, a small clamp blocked the stone, and an abrasive drill was put in contact with one of the edges by applying different loads and angular speeds. The produced powders were collected in disposable weighing boats placed under the abrasive tip. Tests were performed under different experimental conditions (i.e., rotation speed and applied load). According to the TEM analysis performed on the powders, the highest exfoliation degree was obtained by operating at a constant speed corresponding to ca. 3000 rpm and the minimum applied load. A conically shaped drill-bit, made of nickel with embedded white corundum (Al_2O_3) abrasive grains, was selected since it allowed a larger exfoliation area. The conical drill-bit microstructure (see Figure 1) was investigated using a scanning electron microscope (SEM, Quanta 200 FEG microscope, FEI, Hillsboro, OR, USA).

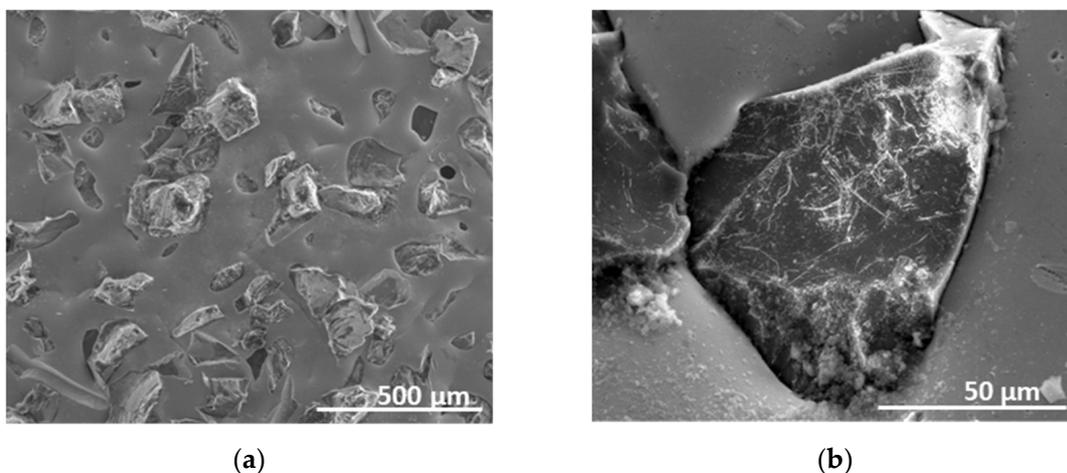


Figure 1. SEM micrographs of the conical drill-bit surface (a) and detail of the corundum abrasive grain embedded in the nickel matrix (b).

According to these SEM micrographs, the abrasive-corundum grains had an average size of ca. one hundred microns. An energy dispersive spectrometer (EDS, FEI Quanta 200 FEG microscope, equipped with EDS, Oxford Inca Energy System 250, equipped with INCAx-act LN₂-free detector, Oxford, UK) was carried out to determine the drill-bit material composition. The cleavage of clinoptilolite nanoplatelets was achieved by the effect of the friction forces acting at the interfaces between the sample and corundum grains. The clinoptilolite single-lamellar crystal morphology was investigated mainly by using a transmission electron microscope (TEM, FEI Tecnai G2 Spirit Twin, operating at 120 kV, equipped with a LaB₆ source and a high-resolution CCD camera, Eindhoven, The Netherlands). Carbon-coated copper grids were used. Such grids were prepared by placing a few drops of a diluted dispersion of clinoptilolite nanoplatelets in ethanol (Aldrich, St. Louis, MO, USA, 96%). To obtain a well-dispersed system, the suspension was

previously sonicated for 10 min and then dried at room temperature. Further morphological information on the clinoptilolite single-lamellar crystals was obtained by comparing the TEM images with SEM micrographs of the same TEM grids.

XPS analysis was performed to identify the mineral's surface chemical properties. XPS has been carried out in an ultra-high-vacuum (UHV) chamber equipped with a non-monochromatized X-ray source (a Mg K α photon at 1253.6 eV) and a VSW HA100 hemispherical analyzer (with PSP electronic power supply and control), leading to a total energy resolution of 0.86 eV. The binding energy (BE) scale of XPS spectra was calibrated using the Au 4f peak at 84.0 eV as a reference. The core-level analysis has been performed by Voigt line-shape deconvolution after background subtraction of a Shirley function.

3. Results and Discussion

The morphology of the single lamellar crystals produced by sample cleavage with an abrasive drill has been investigated using TEM. The TEM micrographs of these clinoptilolite nanoplatelets are shown in Figure 2.

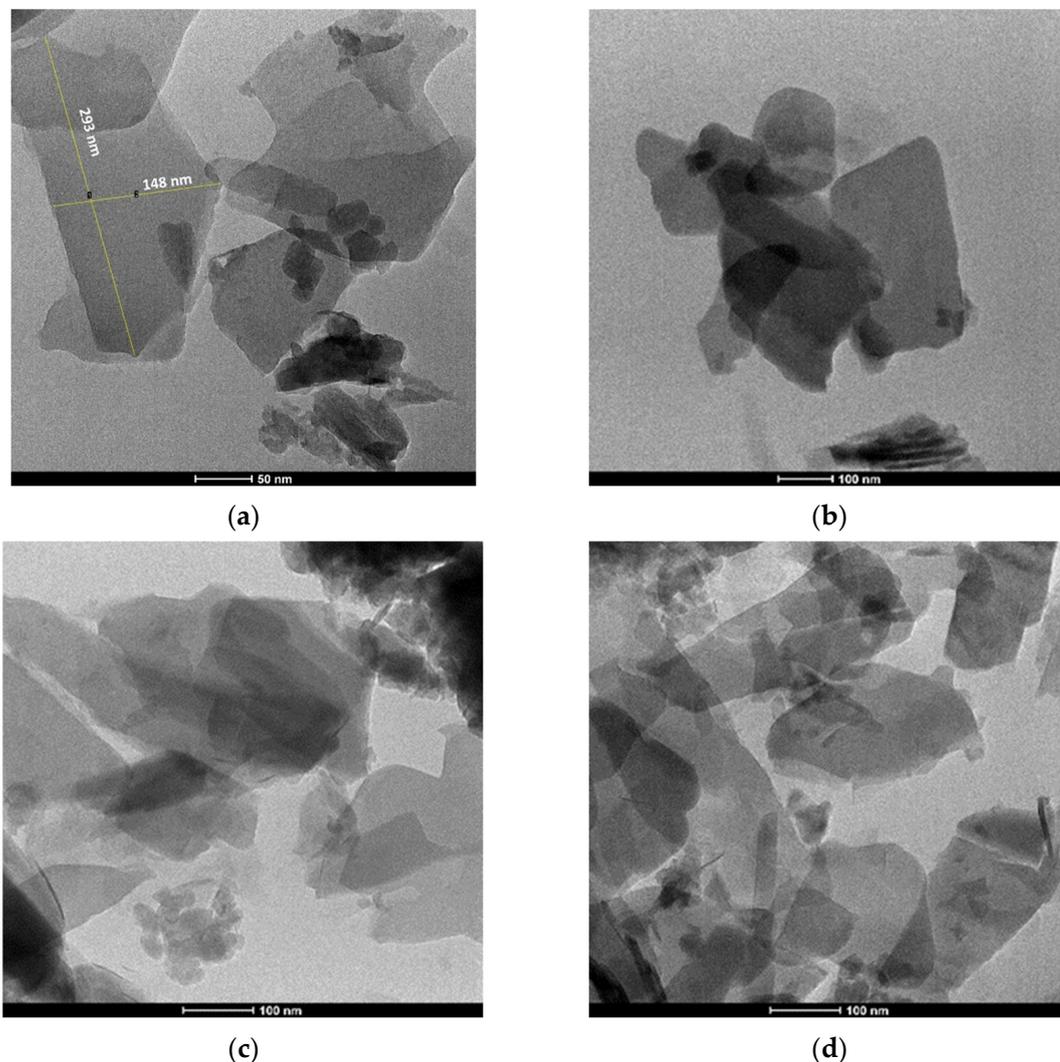


Figure 2. TEM micrographs of small (a) and large (b–d) clinoptilolite lamellar fragments as obtained by the abrasion-drill technology.

The morphological analysis allows a perfect visualization of the aggregate inner structure. Indeed, owing to the low electronic cross-section of Si and Al atoms, these silico-aluminate compounds are semi-transparent to the TEM electron beam. Since the

morphologically investigated aggregates are constituted of platelets with a thickness of 40 nm, the electron beam path in the aggregates is small, preventing beam extinction. In addition, the high magnification of the TEM technique allows a quantitative investigation of such small aggregates, as shown in Figure 2a. The Image J 1.53t software, Bethesda, MD, USA, was used for the analysis. It is also possible to determine the number of lamellae contained in the aggregates based on the grayscale characterizing the image. In fact, as visible in Figure 2, the number of lamellar fragments per aggregate is less than ten. The surface morphology of the exfoliation product has also been investigated by SEM, which has been carried out on the same copper grid previously investigated by TEM. The SEM micrographs of the larger lamellar aggregates, having a diameter varying in the range between 500 nm and 2 μm , are shown in Figure 3a,b.

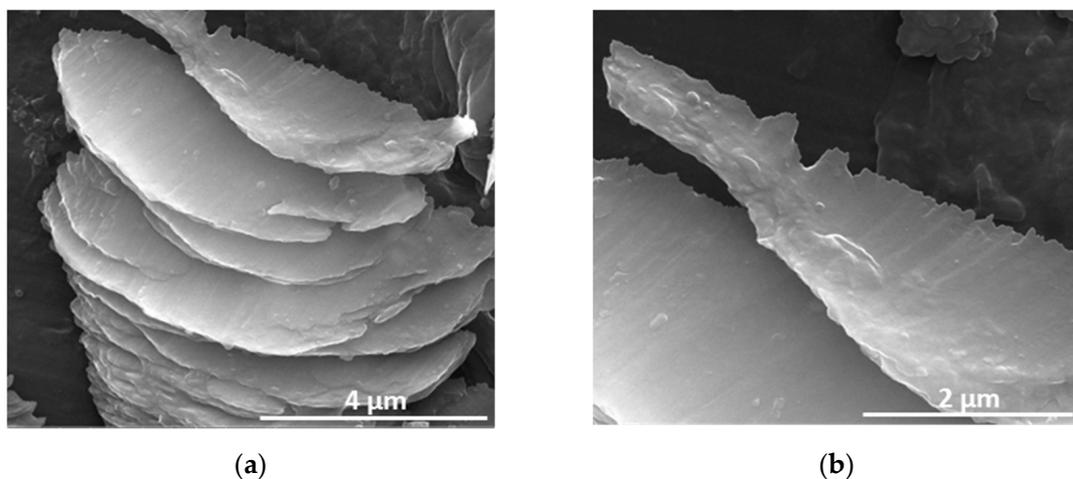


Figure 3. SEM micrographs of lamellar aggregates obtained by the abrasion-drill technology, characterized by a diameter of a few microns (a) and morphological details of a single lamellar crystal (b).

XPS analysis performed on natural clinoptilolite powder revealed the presence of silicon (Si2p core level), aluminum (Al2p), oxygen (O1s), and in lower amounts, calcium (Ca2p), potassium (K2p), and iron (Fe2p) (Figure 4a). All the core levels are shifted in binding energy (BE) due to charging phenomena; thus, taking into account the energy reference from adventitious carbon, we calculated an energy shift of 5.1 eV. Al2p and Si2p BE positions are 74.5 eV and 103.1 eV (main), respectively (Figure 4b,c), in agreement with the literature data [13]. Quantitative analysis leads to the following surface atomic percentages: Si2p (30.8), Al2p (7.2), O1s (59.0), Ca2p (1.0), K2p (1.8), and Fe2p (0.2). In addition, in order to establish the nature of the zeolite sample, the Si/Al atomic ratio was determined, corresponding to 4.3 ± 0.2 , which is compatible with the clinoptilolite form.

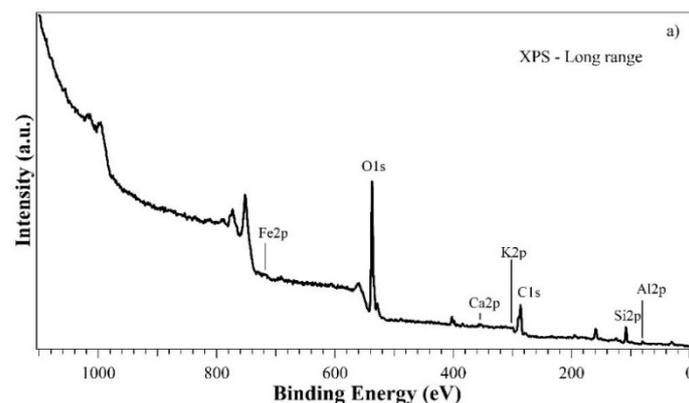


Figure 4. Cont.

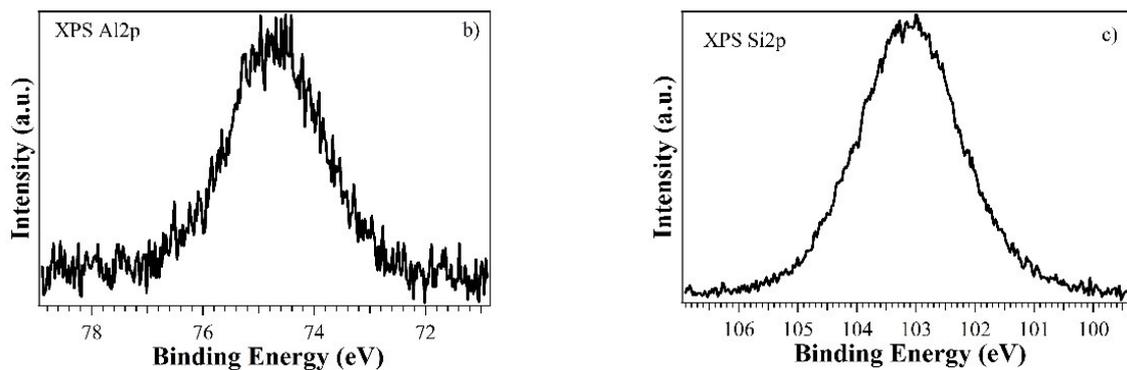


Figure 4. XPS long-range (pass energy 50 eV) spectrum (a) and high resolution (pass energy 20 eV) spectra of Al2p and Si2p core levels (b,c). Natural clinoptilolite was in powdered form.

The surface chemical information has been confirmed by energy dispersive X-ray spectroscopy (EDS) (see Figure 4). Both techniques identify the same elements with comparable relative abundances. However, due to the different probing depths of EDS and XPS, some differences in the Si/Al ratio are expected. According to the EDS results, it has been found that the Si/Al atomic ratio is 5.9 ± 0.3 , which is near the characteristic clinoptilolite value. In addition, owing to the larger K and Ca cation concentrations, this mineral corresponded to clinoptilolite-K,Ca. The complete chemical composition of the sample (i.e., framework and extra-framework elements) can be conveniently represented by the Kiviat chart shown in Figure 5a. As can be seen, the iron and magnesium cations are present at an impurity level.

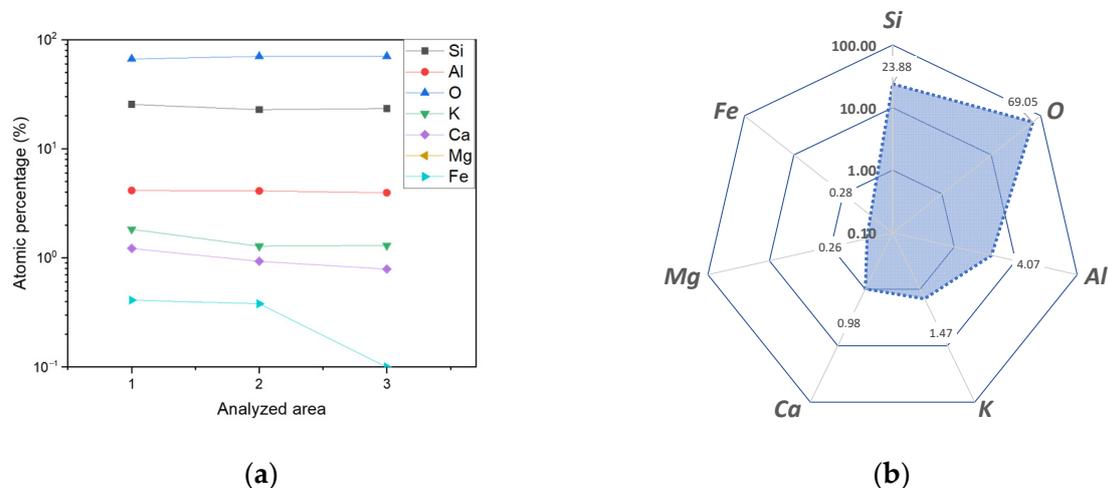


Figure 5. Variation of the elemental composition on the sample surface as measured by EDS analysis (a) and Kiviat chart of the respective average elemental percentage (b).

EDS measurements can also be used to evaluate the natural sample homogeneity by performing the analysis in different areas of the sample surface. The percentage of each element as a function of the analyzed areas on the sample surface is shown in the graph given in Figure 5b. A uniform framework composition characterized the full sample surface, while cation concentrations (especially iron) slightly changed.

4. Conclusions

Clinoptilolite single lamellar crystals and their small aggregates can be obtained by simple abrasion-drill technology. The inner morphological structure of the aggregate has been conveniently investigated by TEM analysis thanks to the low electronic cross-section of the atoms present in the silico-aluminate compound and the thickness of the clinoptilolite

lamellas of only 40 nm. The surface morphology of both single lamellar crystals and their aggregates has also been investigated by SEM. XPS/EDS analysis was performed to determine the compositional information on the studied natural clinoptilolite. According to this analysis, the investigated zeolite sample was potassium-calcium clinoptilolite.

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References

1. Gargiulo, N.; Shibata, K.; Peluso, A.; Aprea, P.; Valente, T.; Pezzotti, G.; Shiono, T.; Caputo, D. Reinventing rice husk ash: Derived NaX zeolite as a high-performing CO₂ adsorbent. *Int. J. Environ. Sci. Technol.* **2018**, *15*, 1543–1550. [[CrossRef](#)]
2. Djaeni, M.; Kurniasari, L.; Purbasari, A.; Sasongko, S.B. Activation of natural zeolite as water adsorbent for mixed-adsorption drying. In Proceedings of the 1st International Conference on Materials Engineering (ICME) and 3rd AUN/SEED-Net Regional Conference on Materials (RCM), Yogyakarta, Indonesia, 25–26 November 2010.
3. Djaeni, M.; Kurniasari, L.; Sasongko, S.B. Preparation of natural zeolite for air dehumidification in food drying. *Int. J. Sci. Eng.* **2015**, *8*, 80–83.
4. Cruz, A.J.; Pires, J.; Carvalho, A.P.; Brotas De Carvalho, M. Adsorption of Acetic Acid by Activated Carbons, Zeolites, and Other Adsorbent Materials Related with the Preventive Conservation of Lead Objects in Museum Showcases. *J. Chem. Eng. Data.* **2004**, *49*, 725–731. [[CrossRef](#)]
5. Sippel, K.H.; Quioco, F.A. Ion-dipole interactions and their functions in proteins. *Protein Sci.* **2015**, *24*, 1040–1046. [[CrossRef](#)] [[PubMed](#)]
6. Bol, R.A.; Harkness, D.D. The Use of Zeolite Molecular Sieves for Trapping Low Concentrations of CO₂ from Environmental Atmospheres. *Radiocarbon* **1995**, *37*, 643–647. [[CrossRef](#)]
7. Li, H.X.; Donohue, J.M.; Cormier, W.E.; Chu, Y.F. Application of zeolites as hydrocarbon traps in automotive emission controls. *Stud. Surf. Sci. Catal.* **2005**, *158*, 1375–1382.
8. Hardie, S.M.L.; Garnett, M.H.; Fallick, A.E.; Rowland, A.P.; Ostle, N.J. Carbon Dioxide Capture Using a Zeolite Molecular Sieve Sampling System for Isotopic Studies (¹³C and ¹⁴C) of Respiration. *Radiocarbon* **2005**, *47*, 441–451. [[CrossRef](#)]
9. Mastinu, A.; Kumar, A.; Maccarinelli, G.; Bonini, S.A.; Premoli, M.; Aria, F.; Gianoncelli, A.; Memo, M. Zeolite Clinoptilolite: Therapeutic Virtues of an Ancient Mineral. *Molecules* **2019**, *24*, 1517. [[CrossRef](#)] [[PubMed](#)]
10. Ivanova, I.I.; Knyazeva, E.E. Micro-mesoporous materials obtained by zeolite recrystallization: Synthesis, characterization and catalytic applications. *Chem. Soc. Rev.* **2013**, *42*, 3671–3688. [[CrossRef](#)] [[PubMed](#)]
11. Kowalczyk, P.; Sprynskyy, M.; Terzyk, A.P.; Lebedynets, M.; Namieśnik, J.; Buszewski, B. Porous structure of natural and modified clinoptilolites. *J. Colloid Interface Sci.* **2006**, *297*, 77–85. [[CrossRef](#)] [[PubMed](#)]
12. Zhang, C.; Huang, Y.; Zhao, H.; Zhang, H.; Ye, Z.; Liu, P.; Zhang, Y.; Tang, Y. One-Pot Exfoliation and Functionalization of Zeolite Nanosheets for Protection of Paper-Based Relics. *ACS Appl. Nano Mater.* **2021**, *4*, 10645–10656. [[CrossRef](#)]
13. Gruenert, W.; Muhler, M.; Schroeder, K.P.; Sauer, J.; Schloegl, R. Investigations of Zeolites by Photoelectron and Ion Scattering Spectroscopy. 2. A New Interpretation of XPS Binding Energy Shifts in Zeolites. *J. Phys. Chem.* **1994**, *98*, 10920–10929. [[CrossRef](#)]

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