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Clays and Zeolites: ancient materials at the forefront of chemistry

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Clays were among the first materials used by mankind. Raw clay has probably always been used for modelling small figures of animals of humans and for building houses. The discovery and control of firing opened the way to the production of dishware and provided a long lasting and resistant building material. The improvements of analytical tools in chemistry during the twentieth century brought about a better understanding of the particular structure of porous silicates, and with it the purpose design of chemical objects where materials properties can be tuned to control reactivity in industrial reactors or to explore elementary reaction mechanisms. Clays and zeolites have accompanied humankind all along its history but they are also parts of the Earth history.

Minerals with a geological life-cycle

As minerals, clays and zeolites appear, live and die in a cycle governed by tectonic movements in the earth mantle.(1,2) Deep under the surface, under very high pressure and temperature, rocks are formed. They are then brought to the surface where they experience completely different conditions, not ideal for them and under which they are not completely stable. When in contact with water and atmosphere these materials undergo deep transformations. The rocky siliceous substrate is altered while it progressively emerges in an oxidizing environment, under low temperature and pressure. In a wet medium, chemical alteration transforms the substrate at its core into secondary minerals. Depending on the acidity and chemical composition of the surrounding aqueous mixture, some components of these minerals will be drawn away and lixiviated. The contents in silicon, aluminum and other metals will change, leading to different families of minerals.

The results form the basis of clays, with very small particles (often below 2μ), with invisible crystals, often lamellar. Surface erosion will draw these fine powders to sedimentary deposits.

These clays can then be buried under more recent deposits, and progressively go back to deeper layers. With increasing pressure, a partial metamorphism can take place (diagenesis) to form mudstones, shales... At greater depths, with tectonic forces, these rocks can in turn be metamorphized into slate or into granites, which will eventually come back to the surface, where they will go through hydrothermal alteration and start the cycle again.

Clays are thus mainly aluminosilicates at very fine granulometry. Their crystal structure is mostly in layers. In the presence of water, these fine particles and these layers will give clays their plasticity. The interlayer space can vary with the water content and with the size of cations located between the layers.

Ubiquitous materials

Clays are of utmost economic importance at the world scale because of their many uses and applications. They can be found in all aspects of our everyday life, from medicine to cosmetics, from paper to dishware, and of course in buildings and agriculture. It would not be possible to overestimate their usage and significance.

The definition of clays is based on their natural origin and on their plastic properties when wet. Most of clays' applications come from their plasticity. The structure of clays remained a mystery during most of their history: the particles of which they are formed are invisible to the naked eye, their crystalline structure was only made clear with modern characterization techniques. They are also complex mixtures.

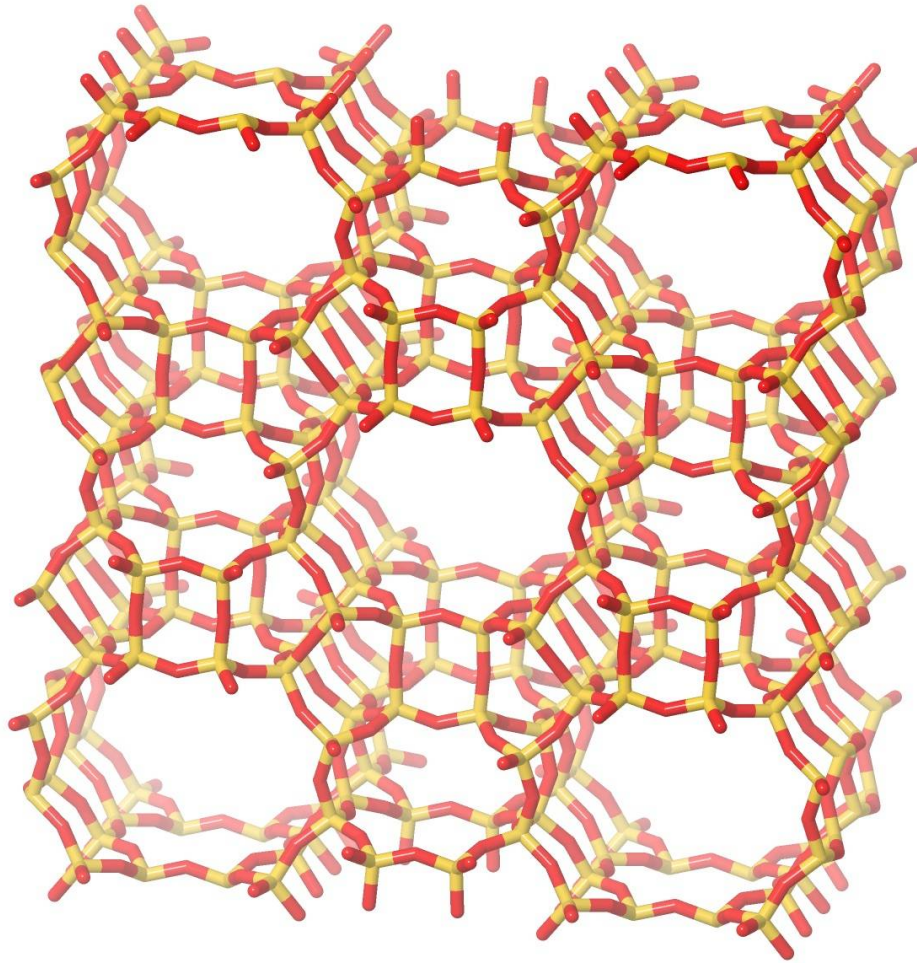
Clays are mixtures of clay minerals together with coarser particles such as sand, with various compositions. Some other aluminosilicates like zeolites can also be found. During the chemical alteration of rocks or during the diagenesis of clays, hydrothermal conditions can lead to the crystallization of new solid phases, not in layers but in a framework of regular channels and cavities: zeolites. Clays and zeolites are thus parent materials, formed by similar processes but under different conditions. Clays are the largest part of the aluminosilicates' family, but zeolites have a unique place, even more for the chemist than for the mineralogist, as we will see later on.

Zeolites often form magnificent macroscopic crystals. They were first described by the Swedish mineralogist Axel Cronstedt in the middle of the eighteenth century. Confronted to this new mineral, as would any analytical chemist of the time, Cronstedt fired it on the burner, and found an unexpected behavior: the rock seemingly boiled. He then coined a new name from the Greek words for "boiling stone".⁽³⁾ With modern techniques, we now know that zeolite are in fact real crystalline sponges, micro (or "nano") porous silicoaluminates.



A natural sample of heulandite and stilbite zeolites (20 cm in its largest dimension). Personal collection of the author.

Zeolites can be considered as a network of molecular-size cavities. They are made by an assembly of silicon and oxygen tetrahedra. Cavities formed in these atomic scaffoldings can range from a few angstroms to 1 or 2 nanometers. These are the exact dimensions for small molecules like water (3 Å). Water, when trapped in a zeolite with the appropriate size, will escape during heating, with the stone itself seemingly boiling.



Schematic structure of the mordenite zeolite. The O atoms (in red) link together the Si or Al atoms (in yellow) forming a framework of tetrahedra. The large channels are visible through this slab of the crystal, they are 7 Å in their largest width. Copyright © 2017 Structure Commission of the International Zeolite Association ([IZA-SC](#))

Cavities in zeolites can accommodate many important molecules for the chemical industry: benzene and other aromatic molecules (6 Å), hydrocarbons... The tight fit between the crystalline host and its molecular guest leads to unique perturbations and new properties, with specific electronic excitations. This is known as chemical confinement and we will come back later to these interactions in nanomaterials.

Zeolites were discovered much later than clays. They were put to great use when large enough sedimentary deposits were found to allow industrial exploitation and when their structures and particular properties were progressively unraveled. Zeolites came to a major place in the chemical industry during the second half of the twentieth century, each of their properties affording new applications. Because of their very large sorption capacity they are great materials for absorbing spillages, for use as chemical reservoirs, as food supplement or as soil improvements in agriculture. Capable of exchanging ions with their environment, they are used as anti-scaling agents or for pollutions remediation. Zeolites can be acidic or basic, with some very strong sites. They can present multiple sites for chemical reactions and are now largely used in catalysis and petrochemistry.

Initially found as natural rocks, most zeolites have been artificially created for technological or scientific purposes. Contrarily to clays, a wide range of zeolites are thus from synthetic origin. Chemists found ways to tune their structure and composition to suit scientific and

industrial needs. These minerals became one of the most significant solid catalysts. Artificial zeolites are used wherever very specific (and wealth generating) applications are considered. The art of synthesizing zeolites with specific properties is a domain that prompts the imagination of contemporary chemists to invent a wide range of porous mineral architectures.

Surface, and sorption capacities

Clays and zeolites are for the chemist, and like any other solid, characterized by their specific surface. When a solid is dipped into a gas or a liquid, molecules circulating in the three dimensions will come to the surface and attach to it more or less strongly. The solid will then be able to sorb a certain amount of these molecules. A perfectly flat surface will rapidly be covered. Benjamin Franklin famously showed that a teaspoonful of oil poured on the surface of a pond in London could cover more than 2000 m².⁽⁴⁾ On a corrugated solid, the rough surface presents holes and bumps which will increase the sorption capacity. When the solid is divided into smaller grains, the number of molecules sorbed on the surface will even increase. One gram of silica, with its fine particles and its highly divided surface, can offer up to 200 m². Porous materials do not only present this external surface: circulating molecules can also sorb inside the pores and cavities. The internal surface can be reached through pores, channels and interlayer space. In some clays and zeolites each gram of dry solid afford 1000 m² of surface with sorption capacity.

It is of course with water in zeolites that the sorption capacity is the most striking. Zeolites have thus been used since the 1950s' for the drying of gas, natural gas and coolant gas.⁽⁵⁾ The sieving properties of the channels in the solid can even improve the drying effect: large molecules like hydrocarbons cannot penetrate the pore system. Very hydrophilic compounds having large molecules will be dried very efficiently by the simple fact that any water they contain gets into the channels easily and is strongly retained in there. Small (mal-) odorous molecules are also very efficiently sorbed and trapped in the channels and cavities of zeolites.⁽⁶⁾ These smell-control capacities make them very popular cat-litters, but also food additives for poultry farming: the solid is mixed with the food as pellets. When ingested, it is quickly loaded with nutrients in the alimentary bolus of the chicken and will only release the nutrients slowly during the digestion, thus increasing their efficiency. The mineral also adsorbs and traps ammonia and other malodorous molecules, leading to less smelly droppings. Added to agricultural soil, these solids can also store water or slowly release fertilizers which will have been added beforehand.

Clays and zeolites are excellent for the remediation of leaks of hydrocarbon or other toxics which they can absorb quickly before they reach the environment.

In zeolites, molecules can only be adsorbed if they can enter and circulate in the pore system which acts as a molecular sieve. This unique property allows the triage of molecules with their size of shape. This has been applied in the industrial process for the separation of linear hydrocarbons.⁽⁷⁾ Molecular sieving is also applied in the separation and purification of gases by tuning the composition and size of the pores in the zeolite crystals. Oxygen concentrators are loaded with zeolites which will selectively sort oxygen from nitrogen molecules for military jet pilots and for medical respirators.

Ions and exchange capacity

Specific surface and shape of the internal channels in the crystal structure thus govern a large part of zeolites' properties. Their chemical composition nevertheless also leads to very specific applications. Clays and zeolites are oxides, crystalline assemblies of oxygen atoms (bearing two formal negative charges) with silicon, aluminum or other metals bringing various positive charges. The resulting crystal can be bearing a neutral charge when opposite contributions balance each other. It is very often not the case and any resulting negative charge must be compensated by cations inserted in the crystalline structure, between the layers of the clay or inside the channels and cavities of zeolites.

These compensating cations are mobile and can be exchanged with other cations. Depending on the natural source of the mineral, the cation content will be different and the "terroir" where these materials originate will have a strong influence. These cations are also a tunable parameter for the chemist to get the exact properties she or he is looking for. The size of the cation itself, for example, will change the available space remaining in the pores and will change the molecular sieving properties of the crystal. Clays and zeolites are common cation exchangers; they can transport cations to release them where needed, in exchange for others.(8)

The most important use of these cation exchangers (in tons) is for water softening. In washing powders, zeolites previously loaded in sodium will release it in the water and trap the calcium and magnesium ions, thus removing lowly soluble carbonates and softening the water for the laundry. Zeolites used in this process are natural additives with relatively low environmental impact.

Water treatment is not limited to softening. Water in swimming pools or in fish hatcheries needs treatment for the removal of ammonia (ammonium) or other charged molecules which could accumulate up to toxic levels. More generally, many pollution remediation processes use ion exchangers. Nuclear power plants produce radioactive ions which can be efficiently trapped by zeolites.(9) Nuclear fuel waste is sometimes stored at the heart of natural zeolite deposits in the ground to improve containment: any leak of radioactive ions would be minimized by the zeolite layer. After Fukushima's nuclear accident, zeolites were deposited around the site to reduce leaking to the sea, and polluted water was treated and filtrated on zeolites.(10) Zeolites were used around Chernobyl and given to the population as food additives in pills or sweets (for children) as a treatment to purify the body from radioactive ions.(11) Zeolites are now commonly sold (unspecified and with no indication on the composition) on the internet for detoxification or purification from possible heavy metals.

Reactive sites for catalysis

By changing the chemical composition of zeolites, reactive sites can be created in their pore system. Molecules entering the pores can then be modified and transformed into products for the chemical industry. The chemical composition is mostly altered by replacing the compensating cations with cations of various degrees of basicity, or even by very strong acidic protons. Metals can also be inserted into zeolites, opening access to the complete landscape of chemical reactivity, from acid-base reactions to oxidations or reductions. Molecules coming in contact with zeolites are sorbed in the pores and reach the active site where they will be modified. Then the modified molecules leave the site and are released in

the external volume. The reaction site itself remains unchanged inside the solid catalyst, ready for the modification of a new molecule.

Solids are very important in catalysis because they provide a surface for the reaction to take place. In the three dimensions of a gas or liquid, two molecules (or the molecule and the reaction site) have a fairly low chance of meeting each other to react together. When the circulation of the molecules is limited to a surface (after sorption), chemical contact and reaction is considerably favored. In the pores of a zeolite, the situation is even more specific: the molecules need to diffuse to the reaction site or to the other molecule before they can react, and only reaction products that can actually form inside the available space, and that can travel back to the external volume, can be obtained. Heterogeneous catalysis on zeolites thus offers size and shape selectivity for producing chemicals that would otherwise be very difficult to obtain.

Zeolites became in the 1960s' the most important industrial heterogeneous catalysts.(12) They brought a complete revolution to oil refining, allowing the use of a much larger fraction of the crude oil through cracking and isomerization reactions. Some zeolites are even used to transform methanol into gasoline, without the need of crude oil itself.(13) Synthetic zeolites are at the basis of catalysis in modern petrochemistry. The ubiquity of these catalysts and the control they allow also lead to their use in biorefineries to convert the complex chemicals from biological sources.(14) It is usually considered that any industrial synthetic material will have met a zeolite at some point in its life.

By performing chemical reactions in the particular environment of the zeolitic pores, new and unexpected phenomena can be observed. When a guest molecule is adsorbed inside a zeolite without water or any other solvent, the zeolite itself plays the role of the solvent and coordinates to the molecule.(15) The zeolite offers the tridimensional environment around the molecule, it can electronically stabilize it and build up hydrogen bonds. Solvation of some organic molecules (3-hydroxyflavone) was shown to be comparable in a zeolite and in methanol.(16) The zeolite can also ionize salts and stabilize the resulting ions.

Water, as any other protic solvent, limits and levels acid strength by its dissociation equilibrium. In the absence of water, protonation reactions in zeolites are not limited to the pH scale and some very weakly basic molecules such as acetonitrile or hydrocarbons can be protonated. Some acidic sites in zeolites are stronger than pure sulfuric acid and are therefore described as superacids.(17) The protonation equilibrium has also been shown to be shifted by temperature.(18) In some molecule-zeolite guest-host pairs, the deformation of the zeolite at high temperature favors the proton transfer and shifts the protonation equilibrium. Acidity is thus not the same at room and at high temperature for this particular acid-base pair. For the guest molecule, the zeolite will seem more acidic at 200°C than at 25°C. This is a strong reminder that it is very important to study catalysts under real reaction conditions rather than in the particular environment (vacuum, low temperature) often needed for characterization techniques.

A most unique aspect of zeolites is the possibility to get molecules inside molecular cages. Such cages can have various electronic or mechanical effects on the confined molecule. That perturbation can completely modify the usual chemical properties. We started to mention acidity, solvation and the influence of temperature, but many other cases were reported.

These effects are similar to the particular state of matter in nanomaterials. Here, the material might be formed of larger particles, but the nano-voids it contains can provide an interesting mirror-image of nanoparticles.

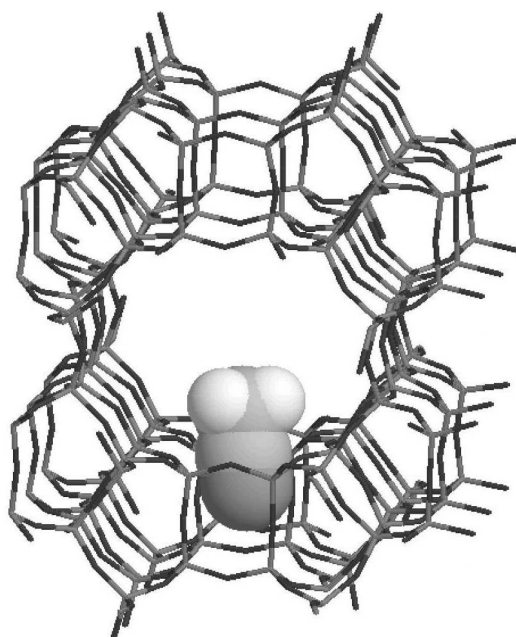
One of the simplest effects of confinement is the protection it can give to reactive and unstable molecules. Lapis Lazuli is a gemstone with a very particular color, forming one of the most ancient and well-known pigments. Ultramarine blue is caused by free radicals on an assembly of three sulfur atoms $S_3^{\cdot-}$. These very reactive radicals would disappear immediately without the constraints of the zeolite cage. Trapped in the small cavities of sodalite, to which they exactly fit, the radicals are protected and produce this uniquely sourced color (at least before a synthetic equivalent was produced in the nineteenth century).(19)

Transition metal complexes have also been trapped in zeolites' pores.(20) They were synthesized by the so-called "ship-in-the-bottle" method where the starting elements are assembled inside the zeolite's internal cavities to form a complex that is too large to escape once it has been formed. The metal complexes can mimic the active center of a natural enzyme. These "Zeozymes" reproduce the chemical behavior of enzymes (natural catalysts), while their mineral matrix protects them against the very harsh conditions needed in a chemical reactor (temperature...). Zeozymes are some sort of hybrid materials between an enzyme and a mineral. Zeolites provide the protective mineral cage but allow access to reactive substrates.

Ideal tools for chemical research

Zeolites can be synthesized as perfect crystals, with no extra-framework phase and very few crystalline defects when they are not damaged during the process of synthesis. They thus provide ideal tridimensional chemical spaces with particular constraints for testing a research hypothesis or a computer model simulating the zeolite to be synthesized.

The containment of a molecule in a small space also leads to an "electronic" deformation of the molecule, more exactly a deformation of its molecular orbitals and a change in their energy levels. Electronic densities are modified all along the molecular backbone of the molecule. A new electric dipole can appear and local electronic affinities can change significantly. When a weakly basic molecule like acetonitrile is introduced in the pore system of the mordenite zeolite (in its acidic form), the molecule will be squeezed between the walls and electrons will accumulate around the nitrogen atoms, which will become more strongly basic. This new electron density will, in its turn, create an electric field and change the electron density in the zeolite walls, increasing their acidity.(21) The acid-base pair becomes much stronger and the proton transfer reaction can take place. This only happens at very specific locations in the pore system, where the fit around the molecule is at its tightest. An empty acidic zeolite, with no water, cations or other molecules in its pores, could be considered as a covalent solid, with very low ionic contribution to its internal bonds. It is by introducing more or less basic molecules that the electronic cloud in the solid is disturbed, ionizing progressively the bonds between the solid and the protons it is bearing and thus creating the Brönsted acidity. The acid strength will increase further with stronger mechanical interaction between the solid and its guest. It is therefore very difficult to determine the acidity of the zeolite on its own. In zeolites, acidity only takes its full meaning within a particular acid-base pair and under particular measurement conditions of temperature and pressure.



The molecule of acetonitrile in the pores of mordenite, from (21).

The limit in space imposed by the pore walls to the guest molecule can constrain its molecular electron orbitals, destabilizing electronic levels.(22,23) Confinement can thus increase the reactivity of molecules. This gives a further advantage to zeolites as heterogeneous catalysts: nano-voids inside the solid lead to many new interesting properties.

Zeolites have deeply modified our approach to materials. This led to new *operando* methods for the characterization of catalysts and functioning materials: studying a material *in situ* is not anymore sufficient and a thorough characterization must now be done while the material is operating, under normal conditions.(24–26) Studying a material under the right conditions of pressure and temperature allows a first description of its chemical state, but it is only with the flow of reactants and the changes in the solid during its operation that we can get a detailed understanding of the living material rather than a static and fixed picture. The living world cannot really be fully understood only on a photographic image: similarly, materials can only be investigated when they are actually operating

Clays and zeolites have been faithful partners of human technology since the dawn of firing techniques and they are still at the cutting-edge of research in the 21st century. Clays have been with us all along our history and they continue to afford a wide range of technological opportunities. Zeolites were identified more recently, but they opened a new era in our understanding of chemistry on, and inside, solids. We have learned to synthesize these materials and tune them to our needs so that they eventually became key actors in chemical science and industry. Zeolites shed new light on nanomaterials, allowing the control of chemical matter at the level of atoms. They have changed the chemists' view of surface: when, in a solid, all internal atoms are accessible to external molecules, what is the difference between the volume of the solid and its tridimensional surface? Chemical concepts are easily pushed to their limits inside zeolites. They are a must for advancing research in chemistry, at the boundary between theoretical concepts and the real-world.

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