

## Zeolites really rock!

Let's start with a quiz:

**Question 1:** What do washing powder, cat litter and blood clotting bandages have in common?

**Answer:** they all contain inorganic solids called zeolites, whose presence is essential for these products to work effectively. **Question 2:** What about industrial processes such as water purification, petrol production and drug synthesis? **Answer:** zeolites play a vital role in all these industrial processes (although they are not actually present in the end products that we purchase). So what are these versatile zeolite materials and what properties do they have that make them so widely used and commercially important?

The secret of zeolites' success in their wide range of uses lies in their well-defined structures. Zeolites are crystalline solids with porous, framework structures built from silicon, aluminium and oxygen. These aluminosilicate structures are very open and contain regular arrays of pores and cavities that can accommodate a wide variety of cations (positively charged ions), such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , as well as small molecules, such as water<sup>1</sup>. Forty-eight zeolites with different



**Fig. 1: Crystals of the zeolite mineral, natrolite**

**[chemical formula:  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2(\text{H}_2\text{O})$ ].**

structures occur naturally as minerals, which are formed when volcanic rocks and ash layers react with alkaline ground water (Fig. 1). In a number of cases, the metal cations in the cavities can be exchanged for others. An interesting mineral where this ability to 'ion exchange' is important is clinoptilolite, which is used to purify wastewater. Heavy-metal cations e.g.  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in polluted water are taken up into the pores of the solid, which can then be filtered off leaving the clean water. This mineral was also used after the Chernobyl

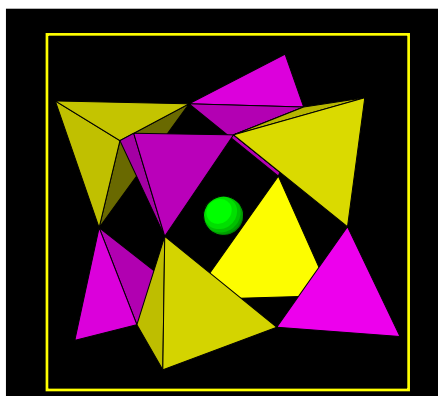
nuclear disaster in 1986 to remove radioactive  $^{137}\text{Cs}$  from drinking water and the solid was also fed to cows and humans in an attempt to decontaminate them (the zeolite minerals themselves are non toxic).

<sup>1</sup> It is the ability of zeolites to lose water from their pores that gave rise to their name. Zeolite minerals were first discovered in 1756 by the Swedish mineralogist, Baron Axel Cronstedt. Cronstedt observed that on heating the white solids over a flame, they hissed and gave off steam as though they were boiling and he named them zeolites from the Greek words *zeo* meaning to boil and *lithos* meaning stone.

Zeolites do not just occur naturally, but can also be synthesised in the laboratory. The aluminosilicate frameworks are made to grow from solution by crystallising around alkali-metal cations or small organic molecules which act as ‘templates’. To date, approximately 150 zeolite structures have been made in this way, many of which are not found in Nature. Synthetic zeolites have an advantage over their natural analogues in that they can be made in a pure state, whereas mineral zeolites are often occur mixed with other minerals, such as quartz. In addition, laboratory syntheses are quicker as they do not (usually!) occur on geological timescales. The preparation of zeolites with new ‘tailor-made’ structures targeted for specific uses is a very exciting and challenging area of chemical research.

### Framework Structures

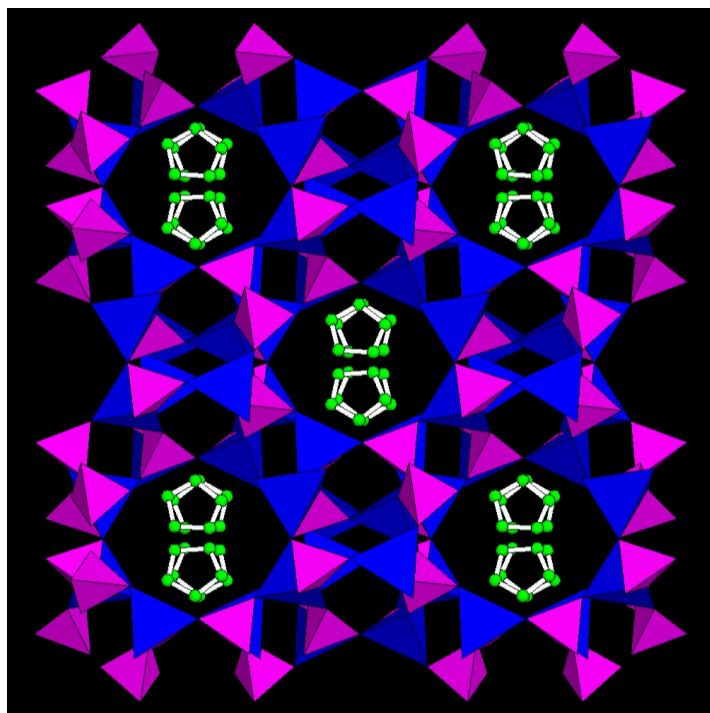
(a)



Zeolite frameworks are assembled from simple tetrahedral building blocks, which have either aluminium or silicon atoms in the middle and oxygen atoms at the corners. The tetrahedra are linked together through their corners in a three dimensional arrangement (Fig. 2). Assembling this molecular tetrahedral-based Lego in different ways can generate a variety of beautiful frameworks. The frameworks contain pores

or linked cavities, which are  $\sim 3 - 20 \times 10^{-10}$  m in diameter ( $\sim$  a few millionths of a millimetre), *i.e.* just the right size to accommodate cations or small molecules. The dimensions of the cavities are of the correct order of magnitude for zeolites to be referred to as ‘microporous materials’.

(b)



**Fig. 2: (a) Tetrahedral building units ( $\text{AlO}_4$  and  $\text{SiO}_4$ ) link through their corners to generate zeolite structures. Here is one type of zeolite cage with a metal cation sitting at its centre.**

**(b) The zeolite called laumontite is found as a mineral and can also be made in the laboratory. Here is the synthetic version, which contains organic molecules in the pores. These pores run all the way through the structure.**

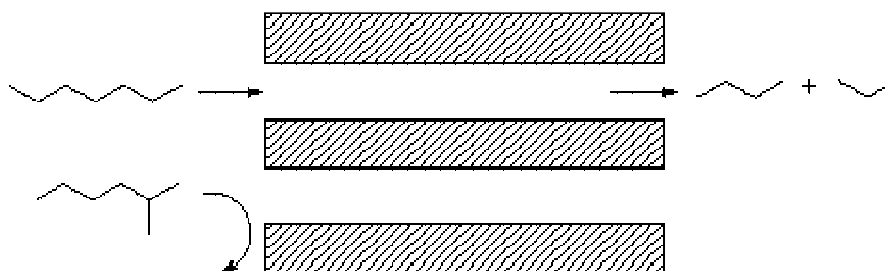
## Uses of Zeolites

The sizes and shapes of the pores are responsible for many of the important applications of zeolites in which they can act as catalysts, molecular sieves and ion-exchange materials – *i.e.* it is the holes in the structures that lead to their interesting properties!

### Zeolites in catalysis

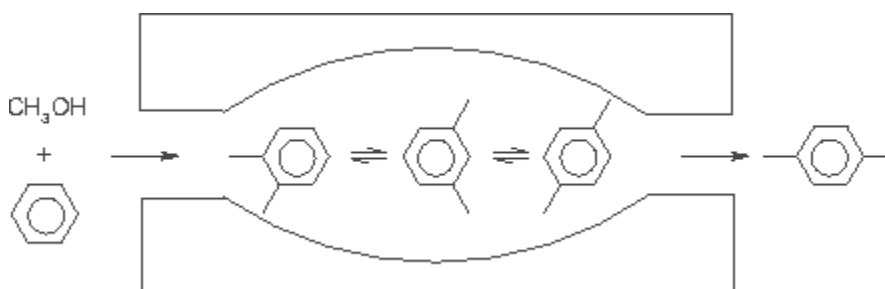
A zeolite can act as a catalyst for a chemical reaction *i.e.* it can speed up the rate of the reaction without being chemically changed at the end of the reaction. The chemical reaction takes place at catalytic sites *within* the pore system of the solid. The shape and size of the pore system therefore determines which reactions can take place in a particular zeolite. Zeolites are therefore said to act as ‘shape-selective’ catalysts. For example, only reactants of a certain size or shape can enter the zeolite pores and reach the catalytic sites and react there. This is illustrated in Fig. 3a, in which a straight-chain hydrocarbon molecule can enter the pore and react, but a branched-chain hydrocarbon cannot. Similarly, only products of a certain size or shape can leave the pores (Fig. 3b) for the preparation of 1,4-dimethylbenzene. A mixture of three products is formed in the cavities, but only one is able to escape.

(a)



**Fig. 3a: Reactant shape selectivity.** Branched-chained hydrocarbons are the wrong shape to enter the zeolite pores. Only straight-chained hydrocarbons can enter and react to form smaller hydrocarbon fragments. These smaller fragments can easily leave the zeolite.

(b)



**Fig. 3b: Product shape selectivity.** Reactants enter the zeolite and react to produce a mixture of products. Only one of these, 1,4-methylbenzene, can diffuse out of the zeolite channels. The other isomers are the wrong shape to leave the pores and so are trapped inside until they react to form the molecule, which can then leave.

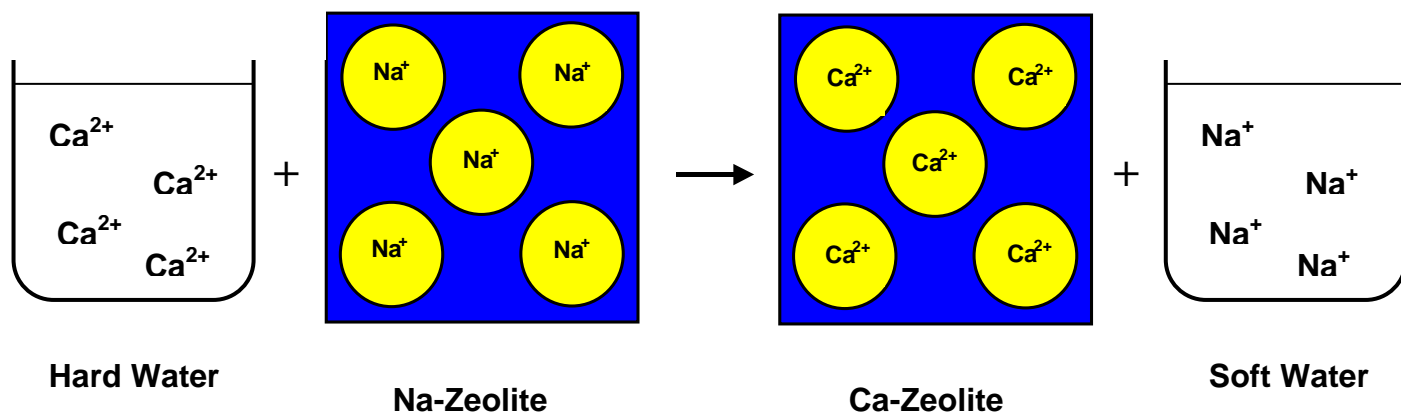
This catalytic behaviour of zeolites is exploited in many commercial applications, which are worth billions of pounds. For example, most of the world's petrol production uses zeolites to crack crude oils (*i.e.* break down the long-chain hydrocarbons present in the oil) to useful short-chain ( $C_1$ - $C_6$ ) molecules. Recently attention has focused on fine-tuning the properties of zeolite catalysts in order to carry out very specific syntheses of high-value chemicals *e.g.* pharmaceuticals and cosmetics.

### **Zeolites as molecular sieves**

Because dehydrated zeolites have very open porous structures, they have large internal surface areas and are capable of adsorbing large amounts of substances. This property, together with their ability to adsorb molecules of certain sizes or shape whilst excluding others (shape selectivity again) has led to them being used as 'molecular sieves'. For example, Zeolite-5A is used commercially for extracting long straight-chain alkanes from hydrocarbon mixtures, which can then be used as the starting materials in the manufacture of biodegradable detergents. Other zeolites are used as odour control agents in cat litter as they can take up ammonia into their framework structures. In addition, because dehydrated zeolites have a high affinity for water they are extensively used as drying agents or desiccants in both industrial and small-scale applications. Bandages used by the US army in the field contain zeolites which when applied to wounds act to dehydrate the blood and accelerate the natural clotting processes. They can also separate gas mixtures, *e.g.* pure medical-grade  $O_2$  can readily be obtained from air.

### **Zeolites as ion-exchange materials**

The alkali-metal cations in zeolites are only loosely held in the pores and they can often readily be exchanged for other types of metal when placed in aqueous solution. This was mentioned above for the cleaning up of radioactive waste. A more widespread use is in water softeners **Fig. 4**.  $Ca^{2+}$  ions are largely responsible for making water hard leading to 'furred' kettles and limescale marks on baths. If a zeolite such as sodium Zeolite-A is added to hard water, the  $Ca^{2+}$  ions enter the zeolite pores where they are 'trapped'. The  $Na^+$  ions are displaced into the water making it soft. The water softener is reusable as it can be regenerated by flushing it with a pure saline solution to replace the calcium cations by sodium cations (a procedure familiar to anyone who has used a dishwasher). Most commercial washing powders also contain ~30% zeolite to soften the water and make the detergent work more efficiently to produce cleaner clothes.



**Fig. 4: A zeolite acting as a water softener. Na-zeolite has  $\text{Na}^+$  in the pores. When it is placed in hard water containing  $\text{Ca}^{2+}$ , the  $\text{Na}^+$  leave the pores and are replaced by  $\text{Ca}^{2+}$ . The  $\text{Na}^+$  is now in the water and makes it soft.**

### **Zeolites may look white but they are also green**

In all, zeolites contribute to a cleaner, safer environment in a great number of ways. Nearly every application of zeolites has been driven by environmental concerns, or plays a significant role in reducing toxic waste and energy consumption. In washing powders, zeolites have replaced harmful phosphate water softeners, now banned in many parts of the world because they cause eutrophication of lakes and seas, leading to the production of algae. Catalysts, by definition, make a chemical process more efficient, thus saving energy and indirectly reducing pollution. Moreover, processes can be carried out in fewer steps, minimising unnecessary waste and by-products. As adsorbents, zeolites can remove atmospheric pollutants, such as engine exhaust gases and ozone-depleting CFCs. As we have seen, they can also be used to remove harmful organics and heavy metal ions and radioactive species from water.

So next time you drive in a car, wash your clothes or drink a glass of filtered water, remember how a product of volcanic eruption has helped you to do this!

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