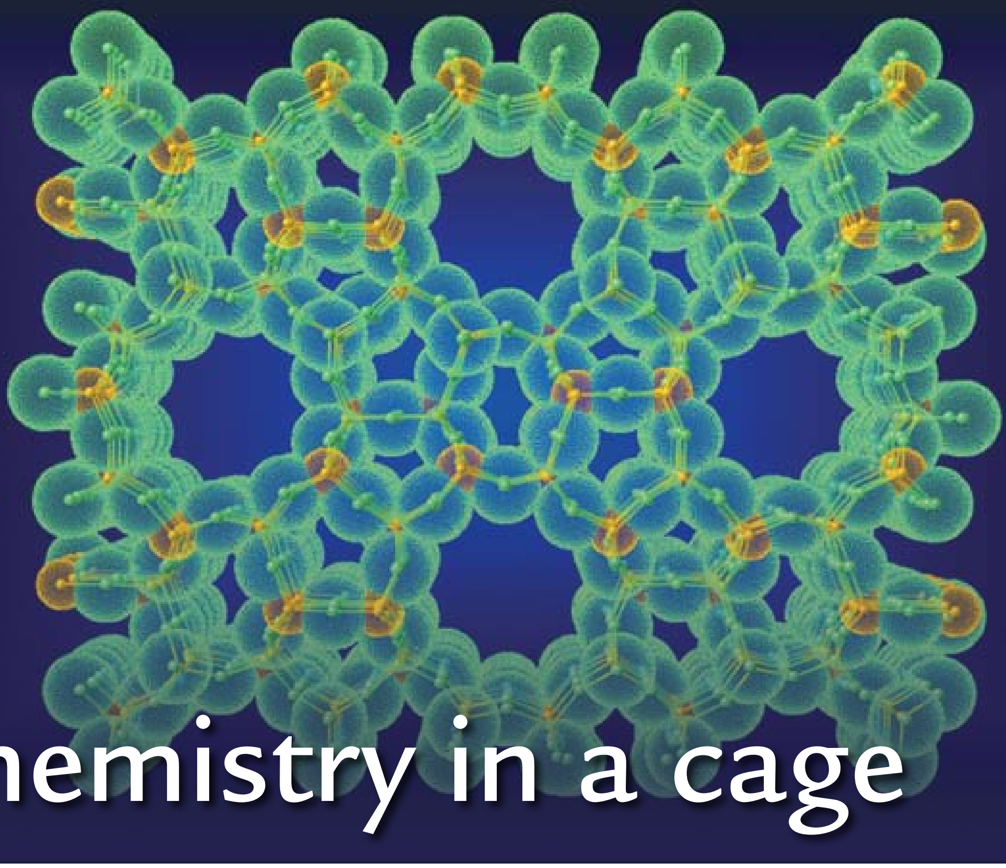

Chemistry in a cage

Sandie Dann and Mark Weller

Figure 1 A typical zeolite structure, showing the tubular spaces between rows of atoms.

Zeolites are sponge-like materials developed from naturally occurring minerals. They have incredibly widespread applications. They are used in consumer products such as washing powder and cat litter while many of the petrochemicals used to make plastics and fibres will have been made using a zeolite. Find out here what zeolites are doing for you!

Atom trapping

Zeolites have diverse but hidden roles in the production and function of many everyday products. Washing powders, petrol, plastic drink bottles and deodorisers are all products which use zeolites directly or in synthesising the chemicals from which they are made. These applications of zeolites depend on their unique structures which, at the atomic scale, have holes and cages like a sponge, Figure 1. These holes or pores can trap molecules and ions and, once they are trapped inside the zeolite, it is often possible for the atoms to rearrange to produce a new, more useful substance.

What is a zeolite?

Many zeolites occur naturally as minerals; the first were described by geologists 250 years ago. Some natural zeolites grow as beautiful crystals (Figure 2); others as seams, thick deposited layers, that can be mined and around 5 million tons are extracted annually. Others are synthetic, made commercially for specific uses where a very pure material is needed or a natural equivalent is rare or non-existent.

Figure 2 Crystals of a naturally occurring zeolite called scolecite

Like many rocks, zeolites are made up of silicon, aluminium and oxygen atoms linked together, Figure 3. Each silicon or aluminium atom is surrounded by four oxygen atoms to form a tetrahedron of composition SiO_4 (or AlO_4); these tetrahedra then share the oxygen atom at each corner with the next tetrahedron. If these tetrahedra link so that there is very little or no space left in the solid then dense structures such as that of the mineral quartz (rock crystal) are produced. However, there are many other ways (it has been calculated there at least 1000 different stable possibilities!) of linking such tetrahedra together to form a three-dimensional network in which there are spaces in the structure called channels and pores (see Figure 3). When these spaces contain small molecules, such as water, the compounds are termed zeolites; they are also sometimes called 'microporous crystalline solids' because they have very small pores (around 1 nm in diameter) that contain ions and molecules. A good way of think of a zeolite structure is as a kitchen sieve shrunk to a millionth of its normal size.

Key words
zeolite
catalysis
ion exchange
hard water
nuclear waste

A nanometre is roughly the size of an atom.

1 nm = 10^{-9} m = 1 millionth of a millimetre

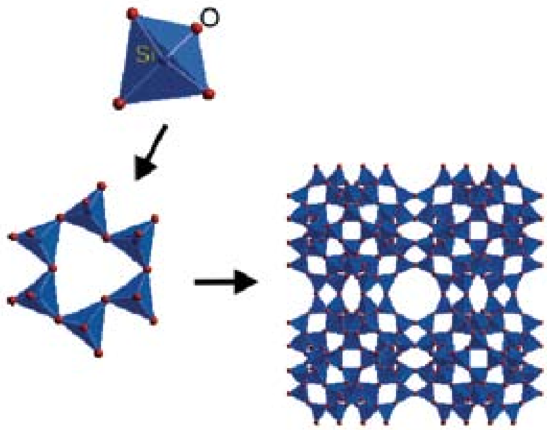

Figure 3 *A single silicate tetrahedron (pyramid) joins with several others to make a pore (hole). These pores then join together to form the extended crystal structure of a zeolite.*

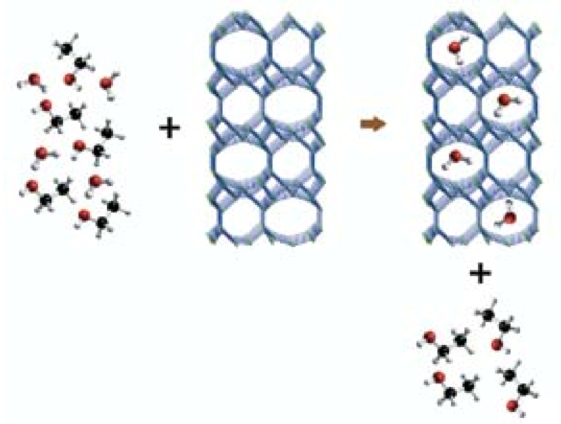

Figure 4 *A zeolite with correctly-sized pores acts as a molecular sieve to trap water.*

Around 200 different zeolites are known: 70 naturally occurring minerals and a further 130 which have been synthesised in research laboratories. Each one has a unique arrangement of the tetrahedra producing different sizes for the cavities and channels in the structure; one of the largest channels has 18 tetrahedra linked together into a ring. This flexibility in their structures leads to a fantastically useful feature of zeolites in that chemists can design them to have pores to undertake a specific function. Also, because the silicon- or aluminium-to-oxygen bonds are strong, these materials are very stable. This means that they can be heated to high temperatures and are only slowly attacked by acids and bases leading to their use in many chemical processes. It is this ability to produce very stable, microporous structures with a variety of different pore sizes that leads to the enormous range of applications.

So how and where are zeolites used?

Molecular sponges and sieves

The size of the micropores in a zeolite is similar to that of many small molecules, such as oxygen, water, ethanol and benzene. By choosing a zeolite with appropriately-sized pores it becomes possible for a molecule to enter the zeolite and then become trapped. In effect the zeolite acts like a sponge and, what's more, a beautifully-designed sponge that can select a single size or type of molecule that just fits inside the holes of that zeolite. This is exploited in applications that use zeolites to dry gases and solvents where a zeolite grabs hold of water molecules, Figure 4. A zeolite is first dried by heating it to 500 °C and any water it contains is driven out of the pores as steam (see the meaning of the word zeolite given on the left). If this dried zeolite is then placed in, for example, a mixture of water and ethanol then just the water molecules can enter the zeolite sponge and the dried solvent, pure ethanol, is left.

The word ***zeolite*** comes from the Greek words ζέιν (zein) meaning to simmer and λίθος (lithos) rock; that is, a rock that simmers. When a zeolite powder is heated it evolves water and particles move as if they are gently boiling.

A similar process can be used to separate gas molecules where the zeolite acts a molecular 'sieve' allowing only one type of molecule to pass into and through its channels. This sort of process can be used to enrich the oxygen content of air to around 90% rather than relying on expensive liquefaction methods.

Zeolites can also be used to trap molecules. In some cases unwanted compounds such as the smelly molecules in urine and sweat can be trapped in the zeolite pores. This is used in some cat litter and odour removal products such as trainer insoles. There are also examples of molecules being temporarily 'stored' in zeolites and later released and there is research underway to try to store hydrogen in this way for future use as an energy source.

Washing powder and nuclear power

If you look at the list of ingredients on a packet of washing powder you will often find zeolite listed. It is there to help produce 'soft' water – that is, water from which calcium and magnesium ions have been removed. This is necessary for the detergent to work well, otherwise these ions attach themselves to the soap molecules that are needed to remove grease from clothing and so reduce their efficiency.

As mentioned above, zeolites usually contain both silicon and aluminium in their structures. The aluminium ions are negatively charged in the zeolite and so for every aluminium ion that is present an additional charge-balancing positive ion is incorporated into the pores. These are normally sodium ions, Na^+. When the zeolite is placed in 'hard' water that contains calcium ions, Ca^{2+}, these exchange places or 'ion-exchange' as the calcium ions have a stronger interaction with the zeolite – so we end up with sodium ions in the water and calcium ions in small particles of zeolite. The effluent produced by softening water in this way is a compound of calcium, aluminium, silicon and oxygen, much the same as many rocks and soils and so is environmentally very safe.

Zeolites are also used to clean up radioactive waste at places such as Sellafield as they are excellent traps for some of the products of the nuclear fission of uranium. In particular caesium and strontium ions in nuclear waste are highly radioactive species which may be grasped with great efficiency by a natural zeolite mineral called clinoptilolite. After the Chernobyl accident this zeolite was fed to livestock, such as sheep and reindeer, to ensure that radioactive ions did not enter the animals' bodies from the gut but were excreted, trapped inside the zeolite pores.

Catalysis

The cracking of crude oil, where it is broken down to produce lighter more useful molecules, is carried out industrially using a zeolite. If the charge balancing cations in the channels of a zeolite are hydrogen ions, H+, rather than sodium or calcium ions, then the zeolites act as very strong acids – much stronger than sulfuric or hydrochloric – and as a result they are sometimes called solid acids. These acidic hydrogen ions attack the long carbon-chain hydrocarbons in crude oil and help break them down into the shorter molecules that are used as petrol or diesel and also in the production of many other petrochemicals such as plastics and man-made fibres.

Zeolites may also be used in a similar process to convert one compound to another, more useful one – a reaction that combines their acid and molecular sieving properties, see Box below.

What next from zeolites ?

As well as developing better catalysts and molecular sieves, zeolites are being studied for storing hydrogen in the next generation fuel cell operated vehicles, for the controlled release of drugs or for producing isolated and environmentally-benign nanoparticles. New zeolites, with different pore sizes, are being developed for many of the applications described above with scientists often still learning from the zeolites that occur in Nature.

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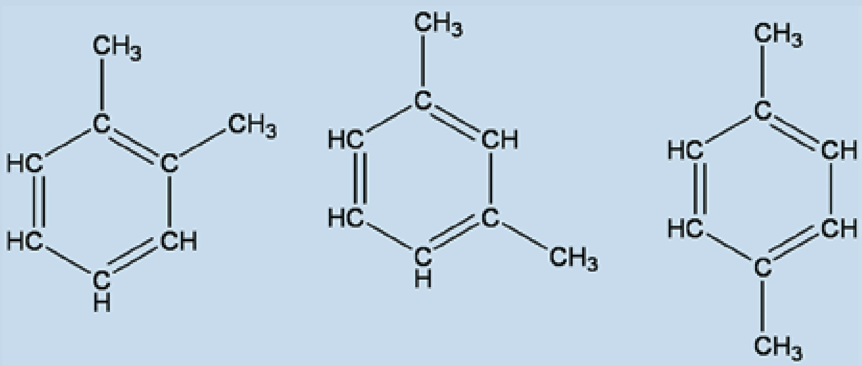
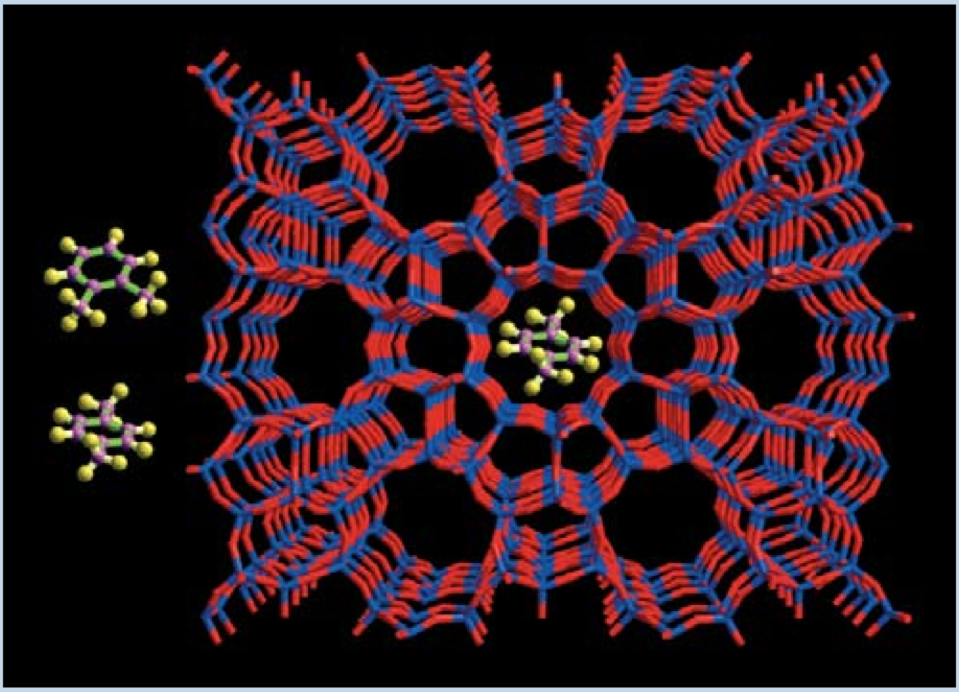
Isomers are compounds with the same formula but a different arrangement of atoms.

Sorting and converting molecules



The compound dimethylbenzene can exist as three isomers – 1,2-, 1,3- and 1,4-dimethylbenzene (left to right in the diagram). Of these, 1,4-dimethylbenzene is much the most desirable compound as it can be oxidized to make terephthalic acid - which is then used to make terylene and PET (polyethylene terephthalate), the plastic used in many bottles.



If a mixture of the three dimethylbenzene isomers is passed through a zeolite known as ZSM-5, then the solid acid permits the three to rapidly interconvert inside its pores. The 1,4 isomer is a narrower molecule than the other two isomers and therefore moves through the zeolite channels faster and can quickly escape (as shown here), while the other two get stuck in the pores where they tend to react further, converting to more 1,4-dimethylbenzene. In this way the isomer mixture is quickly converted to almost pure 1,4-dimethylbenzene!