



CHAPTER 2

LITERATURE REVIEW

Rice husk silica

A. Chemistry of silica^[46]

Silicon dioxide (SiO_2) or silica is the main component of the crust of the earth. Combined with the oxides of magnesium, aluminum, calcium and iron, it forms the silicate minerals in rocks and soil. Silica can be natural or synthetic, crystalline or amorphous.

The building block of silica and silicate structure is the SiO_4 tetrahedron, four oxygen atoms at the corners of a regular tetrahedron with a silicon ion at the center cavity or centroid (Fig. 2.1). The oxygen ion is so much larger than the Si^{4+} ion that the four oxygens of a SiO_4 unit are in mutual contact and the silicon ion is said to be in a *tetrahedral hole*. Natural silica can be crystalline, as in quartz, cristobalite, tridymite, coesite and stishovite, or amorphous, as in opal. Crystalline silica polymorphs are divided according to their framework density (SiO_2 groups per 1000 \AA^3) into pyknosils and porosils, and the latter are further divided into clathrasils and zeosils depending on whether the pores are closed or open, that is, accessible to adsorption.

Table 2.1 Density of crystalline and amorphous silica

Silica	Density (g/mL at 273 K)
Coesite	3.01
α -Quartz	2.65
β -Quartz	2.53
β -Tridymite	2.26
β -Cristobalite	2.21
Amorphous silica	2.20

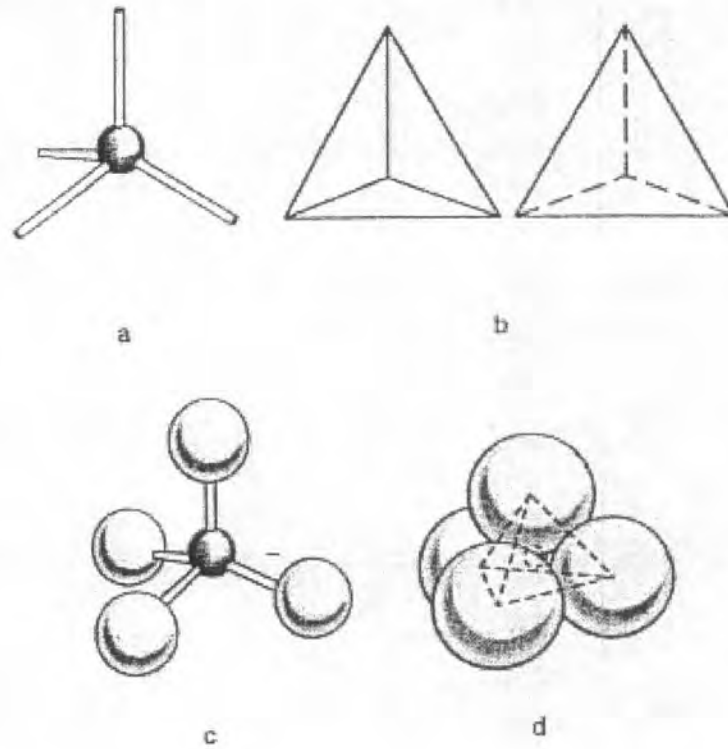


Fig. 2.1 Methods of representing the tetrahedral coordination of oxygen ions with silicon: (a) ball and stick model, (b) solid tetrahedron, (c) skeletal tetrahedron and (d) space-filling model based on packed spheres.

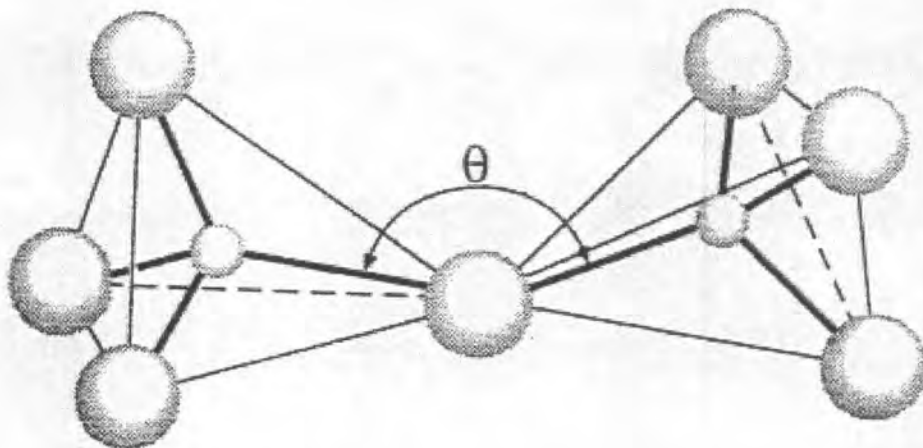


Fig. 2.3 Schematic representation of adjacent SiO_4 tetrahedral that shows the Si-O-Si bond angle. Small circle, Si; Large circle, O.

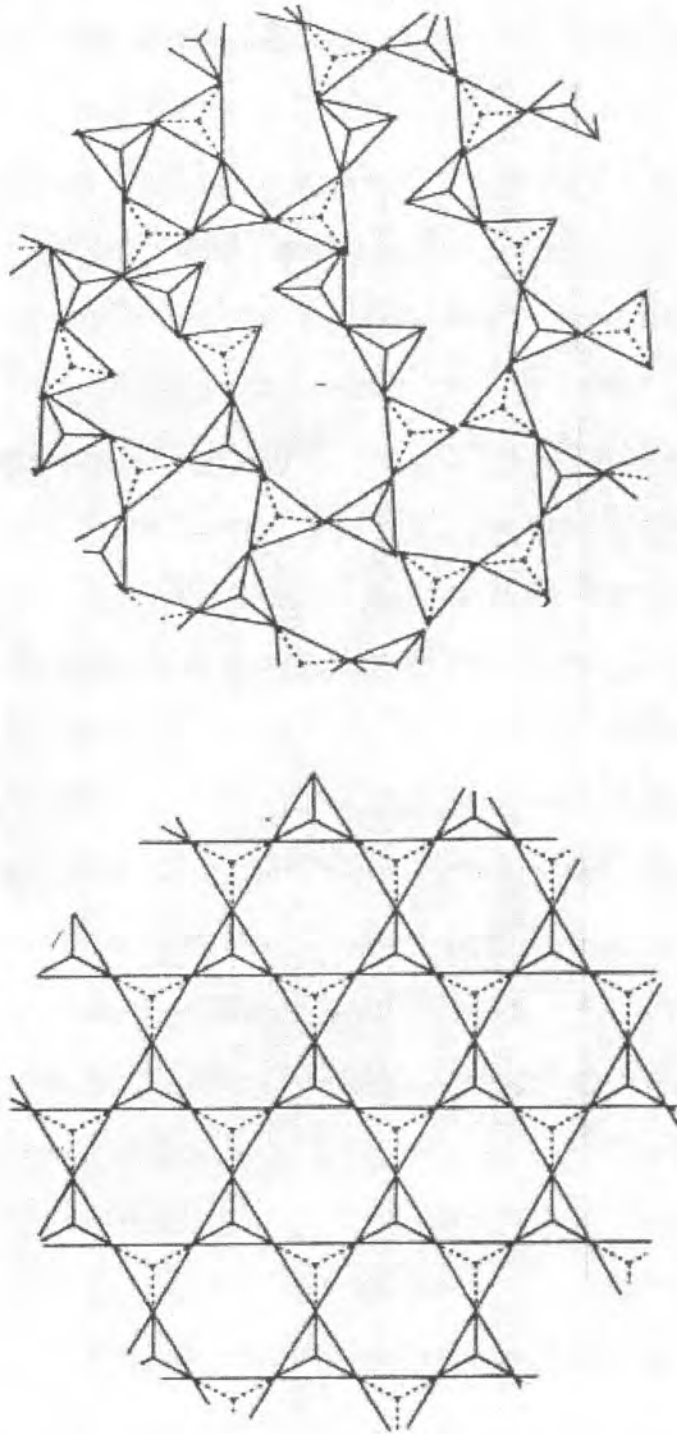


Fig. 2.2 Two-dimensional representation of random versus regular packing of $(\text{Si-O}_4)^{4-}$ tetrahedral: amorphous (a) and crystalline silica (b).

Familiarity with the structure of crystalline silica is helpful in understanding the bulk and surface structure of amorphous silica. All forms of silica contain the Si-O bond, which is the most stable of all Si-X element bonds. The Si-O bond length is about 0.162 nm, which is considerably smaller than the sum of the covalent radius of silicon and oxygen atoms (0.191 nm). The short bond length largely accounts for the partial ionic character of the single bond and is responsible for the relatively high stability of the siloxane bond. Although in most silica and silicates the silicon atom is surrounded by four oxygen atoms, forming the tetrahedral unit $[\text{SiO}_4]^{4-}$, a sixfold octahedral coordination of the silicon atom has also been observed in stishovite and coesite. The arrangements of $[\text{SiO}_4]^{4-}$ and $[\text{SiO}_6]^{8-}$ and the tendency of these units to form a three-dimensional framework structure are fundamental to silica crystal chemistry.

The silicates are built up in a manner analogous to that of the polyborates and the polyphosphates by sharing of oxygen atoms. In practice, two different SiO_4 groups may share only one oxygen atom, but any or all of the four of the oxygen atoms on a SiO_4 group may be shared with adjacent groups. Sharing of two oxygen atoms per unit yields a *chain*, three oxygen atoms a *sheet* and four oxygen atoms a *three-dimensional network*. The crystalline silica quartz, tridymite and cristobalite are in truth network silicates, each silicon being bound to four oxygen atoms and each oxygen being bound to two silicon atoms. Quartz is the stable form of crystalline silica below 870 °C, tridymite below 1470 °C and cristobalite below 1710 °C but either of the two high-temperature forms can exist for long period of time at room temperature and atmospheric pressure without turning to quartz.

The polymorphism of silica is based on different linkages of the tetrahedral $[\text{SiO}_4]^{4-}$ units. Quartz has the densest structure, and tridymite and cristobalite have a much more open structure. All three forms exist in α - and β -forms, which correspond to low- and high-temperature modifications, respectively. The α - and β -modifications differ only slightly in the relative positions of the tetrahedral arrangements. This similarity is evident from the fact that the conversion $\alpha \leftrightarrow \beta$ is a rapid displacing transformation that

occurs at relatively low temperatures. Quartz is the most stable modification at room temperature; all other forms are considered to be metastable at this temperature.

In amorphous silica the bulk structure is determined, as opposed to the crystalline silica, by a random packing of $[\text{SiO}_4]^{4-}$ units, which results in a nonperiodic structure (Fig. 2.2). As a result of the structural differences the various silica forms have different densities (Table 2.1).

The structure, Si-O bond length, and Si-O-Si bond angle in crystalline and amorphous silica have been studied by X-ray, electron and neutron diffraction and by infrared spectroscopy. Three strong adsorption bands at 800, 1100 and 1250 cm^{-1} measured by infrared transmission techniques are attributed to fundamental Si-O vibrations and do not differ greatly in the various silica modifications, whereas in the high frequency region (2800-4000 cm^{-1}) certain distinct differences are observed. Fig. 2.3 is a schematic representation of adjacent SiO_4 tetrahedral that shows the Si-O-Si bond angle. Diffraction measurements have shown a difference between the Si-O-Si bond angle of quartz (142°), cristobalite (150°) and fused quartz (143°).

B. Rice husk ash

Rice husk, a major agricultural waste, is the natural sheath that forms on rice grains during its growth. During the rice milling process, rice husk is removed from the grain to create white rice. A large quantity of rice husk which is known to have fibrous materials with high silica content^[47]. The major constituents of rice husk (Table 2.2) are inorganic ash varying from 13-29 wt % and organic matters composed of cellulose, lignin and sugar. The elemental analysis of these organic matters is 51 wt% carbon, 7 wt% hydrogen and 42 wt% oxygen^[48]. During growth, rice plants absorb silica from the soil and accumulate it into their structures. Sharma et al. have performed a mapping of the silica distribution in the rice husk by energy-dispersive X-ray analysis (EDAX), and they have shown that it is concentrated primarily within the outer epidermis (Fig. 2.4a), although a small amount of silica was found within the inner epidermis (Fig. 2.4b)

adjacent to the rice kernel^[49]. This silica is concentrated by burning at high temperature removing other elements, which make the ash so valuable.

Table 2.2 Organic and inorganic matter in rice husk^[50]

Component	wt %
Ash	13-29
Cellulose	34-44
Lignin	19-47
Sugar*	17-26

*D-xylose, L-arabinose, Methylglucuronic acid and D-galactose.



Fig. 2.4 SEM micrographs of outer epidermis (a) and inner epidermis of rice husk (b).

Rice husk ash (RHA) is a general term describing all types of ash produced from burning rice husk. The burning of rice husk in air results in the formation of RHA with a content in SiO₂ that varies from 85 to 98% and some amount of metallic impurities (such as Na⁺, K⁺, Ca²⁺, Mn²⁺ and Mg²⁺ cations) depending on the burning conditions, furnace type, rice variety, rice husk moisture content, climate, geographic area^[19], soil and the use of fertilizers. Silica in RHA undergoes structural transformations depending on the burning temperature. The burning at moderate temperatures (550-700 °C) amorphous silica is formed. At high temperatures (>700 °C), these usually lead to the crystallization of amorphous silica to crystalline silica (cristobalite and tridymite)¹.

C. RHA applications

Addition to high silica content, RHA is highly porous and lightweight, with a very high external surface area. Due to its valuable properties RHA is useful for many industrial applications. An extensive literature search has many uses of RHA including:

1. Cement industry

Substantial research has been carried out on the use of amorphous silica in the manufacture of concrete. There are two areas for which RHA is used, in the manufacture of low cost building blocks and in the production of high quality cement. Ordinary Portland Cement (OPC) is expensive and unaffordable to a large portion of the world's population. Since OPC is typically the most expensive constituent of concrete, the replacement of a proportion of it with RHA offers improved concrete affordability, particularly for low-cost housing in developing countries. The addition of RHA to cement has been found to enhance cement properties:

- The addition of RHA speeds up setting time, although the water requirement is greater than for OPC.
- At 35% replacement, RHA cement has improved compressive strength due to its higher percentage of silica.
- RHA cement has improved resistance to acid attack compared to OPC, thought to be due to the silica present in the RHA which combines with the calcium hydroxide and reduces the amount susceptible to acid attack.
- More recent studies have shown RHA has uses in the manufacture of concrete for the marine environment. Replacing 10% Portland cement with RHA can improve resistance to chloride penetration.
- Several studies have combined fly ash and RHA in various proportions. In general, concrete made with Portland cement containing both RHA and fly ash has higher compressive strength than concrete made with Portland cement containing either RHA or fly ash on their own.

RHA can also replace silica fume in high strength concrete. Silica fume or micro silica is the most commonly used mineral admixture in high strength concrete. The major characteristics of RHA are problems RHA needs to be ground finely into particles of 8-10 μm and a superplasticizer added to reduce water requirement.

2. Steel industry

RHA is used by the steel industry in the production of high quality flat steel. Flat steel is a plate product or hot rolled strip product, typically used for automotive body panels and domestic 'white goods' products. RHA is an excellent insulator, having low thermal conductivity, high melting point, low bulk density and high porosity. Its insulating properties that makes it an excellent 'tundish powder'. These are powders that are used to insulate the tundish, prevent rapid cooling of the steel and ensure uniform solidification in the continuous casting process.

3. Other less wide spread uses have also been identified:

- Due to its insulating properties, RHA has been used in the manufacture of refractory bricks.
- There are reports of RHA being used in the manufacture of lightweight insulating boards in developing countries.
- Several studies have been carried out to purify RHA for use in silicon chip manufacture. The techniques are still being developed, but appear promising.
- It is known that farmers in Asia will use RHA to prevent insect in stored food stuffs, and several scientific studies have been carried out to test the efficiency of this.
- Greenwich University is researching small-scale paddy milling in Bangladesh and Vietnam, and the possibility of using RHA for water purification.
- A company in the USA has produced a prototype plant for manufacturing activated carbon from RHA, and the major market for this is in water purification.

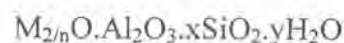
- There are several reports detailing the use of RHA in vulcanizing rubber, although in small scale experiments.
- There are reports of RHA being used as a soil ameliorant to help break up clay soils and improve soil structure.
- Rice husk burnt slowly over a period of six months have been found to be effective as oil absorbent and are marketed in California.

Zeolite molecular sieves^[3]

A. Zeolite structure and classification

In 1932 McBain proposed the term “molecular sieve” to describe a class of materials that exhibited selective adsorption properties. He proposed that for a material to be a molecular sieve, it must separate components of a mixture on the basis of molecular and shape differences. Two classes of molecular sieves were known when McBain put forth his definition: the zeolites and certain microporous charcoals. The list now includes the silicates, the metasilicates, metalloaluminates, the $AlPO_4$'s, and silico- and metalloaluminophosphates, as well as the zeolites. The different classes of molecular sieve materials are listed in Fig. 2.5. All are molecular sieves, as their regular framework structures will separate components of a mixture on the basis of size and shape. The difference lies not within the structure of these materials, as many are structurally analogous, but in their elemental composition. Therefore, all are molecular sieves though none but the aluminosilicates should carry the classical name, zeolite.

Zeolite is a crystalline aluminosilicate with a framework based on an extensive three-dimensional network of oxygen ions. Situated within the tetrahedral sites formed by the oxygen can be either a Si^{4+} or an Al^{3+} ion. The AlO_2^- tetrahedra in the structure determines the framework charge. This is balanced by cations that occupy nonframework positions. A representative empirical formula for zeolite is written as:



M represents the exchangeable cations, generally from the group I or II ions, although other metal, nonmetal, and organic cations may also be used to balance the framework charge, and n represents the cation valence. These cations are present either during synthesis or through post-synthesis ion exchange. The value of x is equal to or greater than 2 because Al^{3+} does not occupy adjacent tetrahedral sites. The crystalline framework structure contains voids and channels of discrete size. The pore or channel openings range from 3 Å to 8 Å, depending on the structure. Water molecules present are located in these channels and cavities, as are the cations that neutralize the negative charge created by the presence of the AlO_2^- tetrahedral in the structure. Typical cations include: the alkaline (Na^+ , K^+ , Rb^+ , Cs^+) and alkaline earth (Mg^{2+} , Ca^{2+}) cations, NH_4^+ , H_3O^+ (H^+), TMA^+ (tetramethylammonium) and other nitrogen-containing organic cations and the rare-earth and noble metal ions

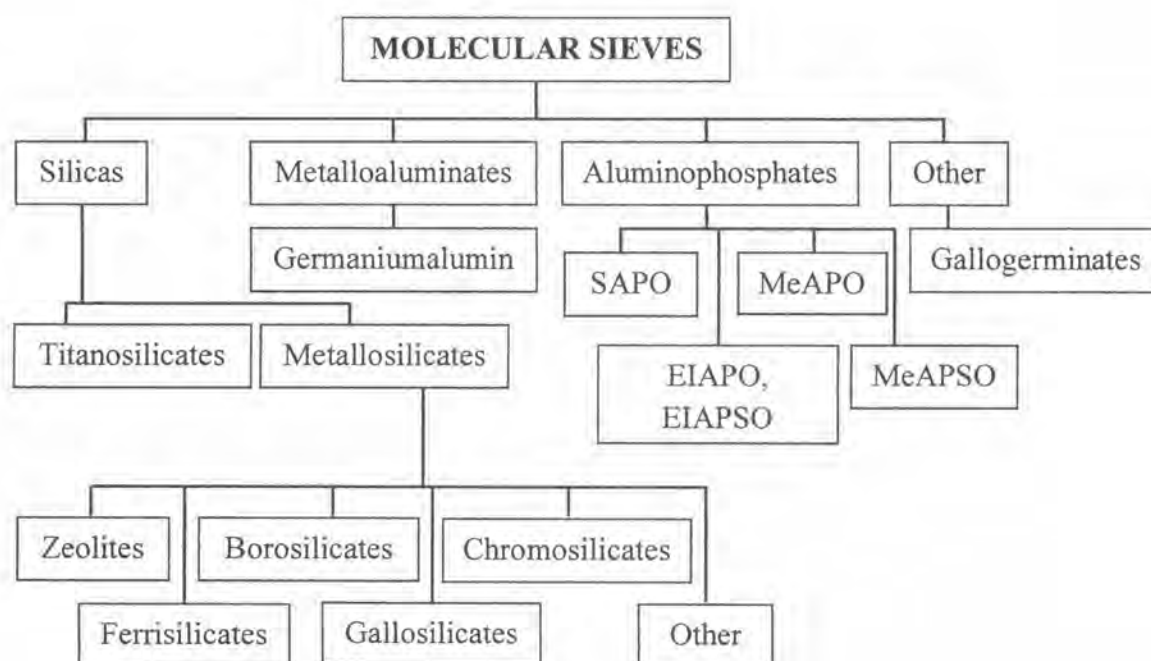


Fig. 2.5 Classification of molecular sieve materials indicating the extensive variation in composition.

Loewenstein has formulated certain rules (Loewenstein's rule) that may govern the linking together of silica tetrahedral and of the tetrahedral and octahedra of alumina. The distribution of tetrahedra in a crystal is not entirely random in amorphous and crystalline aluminosilicates.

(i) Whenever two tetrahedra are linked by one oxygen bridge, the center of only one of them can be occupied by aluminum; the other center must be occupied by silicon or by another small ion of electrovalence 4 or more, such as phosphorous.

(ii) Whenever two aluminum ions are neighbors to the same oxygen anion, at least one of them must have a coordination number larger than 4, that is, 5 or 6, toward oxygen.

These rules explain the maximum substitution of 50 percent of the silicon in three-dimensional framework networks of tetrahedral by aluminum. For 50 percent substitution, rigorous alternation between silicon and aluminum tetrahedral becomes necessary. To date no deviation from these rules has been observed in the zeolite systems, the aluminophosphates or the metasilicates studied.

The fascinating properties of zeolitic materials essentially originate from their structures. The lack of proper identification techniques hindered longtime the determination of structures, explaining the slow progress made in the century following their discovery. The invention of X-ray diffraction at the beginning of the 20th century to probe the structural properties of materials initiated systematic studies on zeolite identification. A zeolite topology concept was introduced. It corresponds to the connectivity of the tetrahedra of the framework through line segments and nodes and represents the highest possible symmetry. The structure commission of the International Zeolite Association (IZA) provides up to date classification by framework type^[33]. For example, two important and industrially relevant structures are depicted in Fig. 2.6.

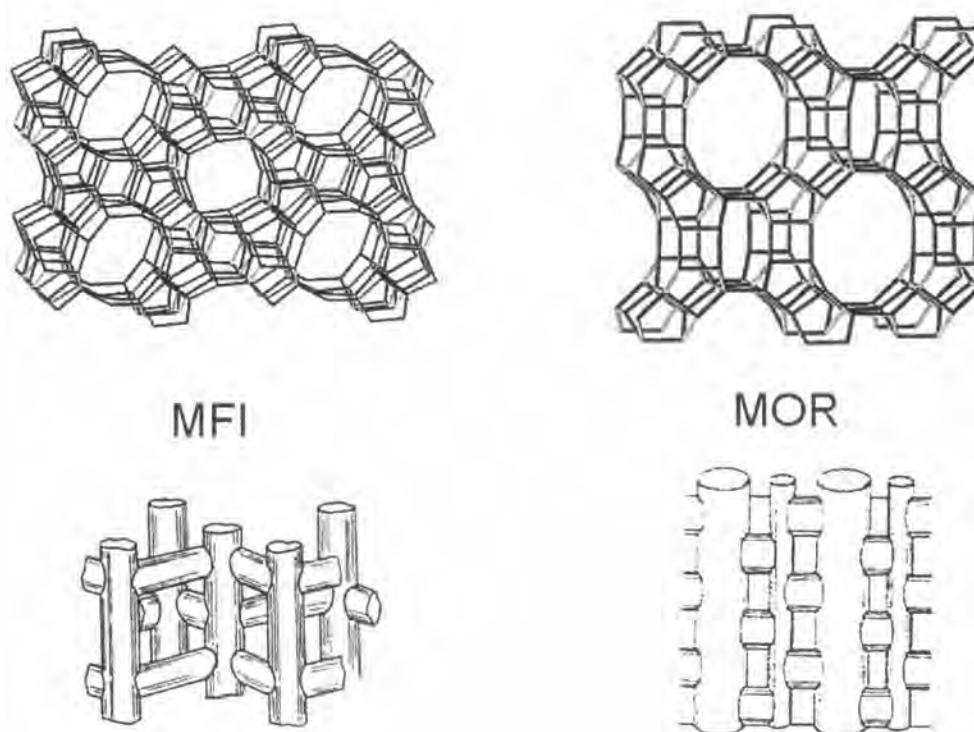


Fig. 2.6 Two examples of zeolite framework and pore system: MFI and MOR topologies.

The large majority of zeolite structures are constructed by repeating so-called secondary building units (SBUs). Another way to classify zeolites is to take into account their pore openings and dimensionality of their channels. Thus, one distinguishes small pore zeolites (eight-membered-ring pore), medium pore zeolites formed by ten-membered rings and large pore zeolites with twelve-membered-ring pores. This classification simplifies comparisons in terms of adsorptive, molecular sieving and catalytic properties. The different ring sizes, based on the different number of T atoms (T = Si or Al) define the pore opening, are shown in Fig. 2.7, for three representative zeolites: erionite, ZSM-5 and zeolite Y.

1. Secondary building unit

Describing zeolites in terms of their pore openings and channel systems simplifies comparisons of their adsorptive and catalytic properties. The need to comprehend, or at least relate, the seemingly large number of complex zeolite structures in order to compare structural properties has led to the development of structural building units. These units are also used in efforts to understand the way that individual structures form from the complex mixtures used in their synthesis.

The primary building unit of a zeolite structure is the individual tetrahedral TO_4 unit (Fig. 2.8), where T is either Si or Al. A secondary building unit (SBU) consists of selected geometric groupings of those tetrahedra. In SBU Si or Al is present at each corner or termination but the oxygens are not shown. They are located near the mid-points of the lines joining each pair of T atoms. Meier in 1967 proposed the SBU as the smallest number of such units from which then known zeolite topologies could be built. There are nine such building units, which can be used to describe all of the known zeolite structures. These secondary building units consist of 4, 6 and 8-member single rings, 4-4, 6-6 and 8-8-member double rings, and 4-1, 5-1 and 4-4-1 branched rings. The topologies of these units are shown in Fig. 2.9. Also listed are the symbols used to describe them. Most zeolite frameworks can be generated from several different SBUs.

(b) Extended chain building unit

The secondary building unit does provide a convenient method of topologically describing and relating different zeolites. However, in many instances describing structural differences and similarities requires a building unit that takes into account the arrangement of these secondary building units in space. The chain building unit adds further dimension to the building unit. For example, when we look at the tetrahedral that comprise the 4-member ring building unit, it is immediately obvious that there is more than one way of joining together the 4 ring building units. There are in fact four unique orientations for the tetrahedral in the 4 ring. All four tetrahedral can be pointing up (or all four pointing down), two adjacent can be pointing up with the other two pointing down, the two opposite tetrahedral can be pointing up, or three can be pointing up. The linking,

therefore, of these 4 rings to form the chain building unit results in four completely different sequences for the tetrahedra.

The use of the extended chain composed of the secondary building unit simplifies visualization of certain aspects of the zeolite structures. Most notable of these is the recognition and description of an intergrowth of one zeolite within another.

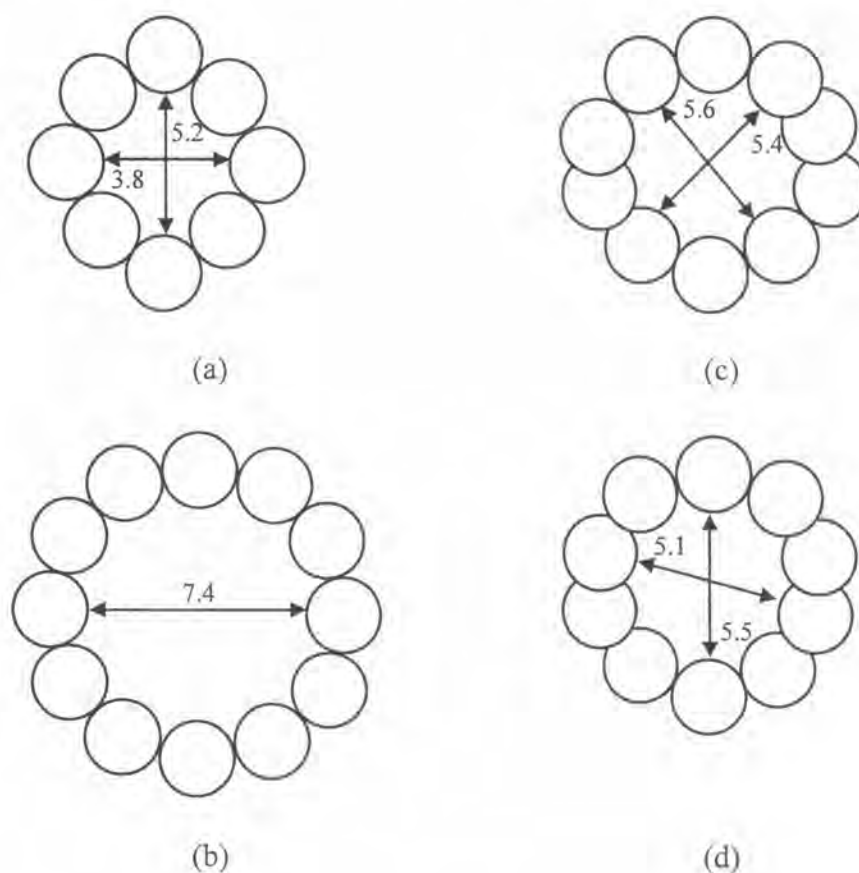


Fig. 2.7 Examples of the three types of pore openings in the zeolite molecular sieves.

- (a) Erionite contains an 8 ring pore opening
- (b) Zeolite Y contains a 12 ring pore opening
- (c) ZSM-5 10 ring (straight channel)
- (d) ZSM-5 10 ring (Sinusoidal channel)

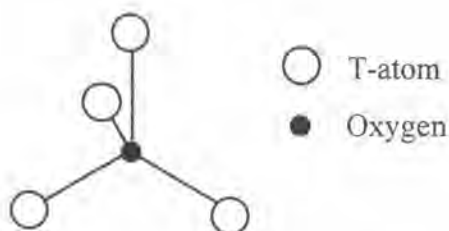


Fig. 2.8 The tetrahedral TO_4 unit.

(c) Sheet building unit

An alternative method for describing extended zeolite structures uses the sheet building unit. Here we do not visualize a zeolite using a one dimensional chain unit; instead, a two-dimensional sheet unit from which the framework structure is generated through attaching layers is helpful in visualizing the complex structures.

Various other ways of formulating zeolite framework topologies have been developed, involving structural units of greater complexity than the SBU of Fig. 2.9. These ways include^[4]:

(i) Stacking of polyhedral cages with other cages, like or unlike the first, with appropriate co-ordination numbers among the cages. The stacked polyhedral share faces with other polyhedral.

(ii) Stacking of aluminosilicate layers of a given kind in a number of layer sequences and with appropriate T-O-T (T = Al or Si) bonds cross-linking each pair of layers. The layers may be of a number of kinds often puckered to give different configurations.

(iii) Cross-linking chains of a given type to other parallel chains of the same kind, by Si-O-T bonds. This may be done in a variety of ways, and the chains can be of a number of different kinds.

(iv) By the action of an n-fold operator axis upon chains placed alongside the axis. The chains may be puckered to give different configurations. This is easily

visualized for the ladder-like chains of 4-rings found in the phillipsite structure or in feldspars.

(v) Through the so-called “sigma transformation”. This is a conceptual device which refers to the expansion of the single tetrahedron, TO_4 , or of a tetrahedrally connected structure by imaginary fission of T atoms lying on specified planes or surfaces running through the structure, and creation of new oxygen bridges connecting the pairs of T atoms resulting from the fission.

The above ways of generating structures may be regarded as typical. By indicating structural relationships between framework topologies they assist in the placing zeolites into the sub-divisions or groups shown in Table 2.4.

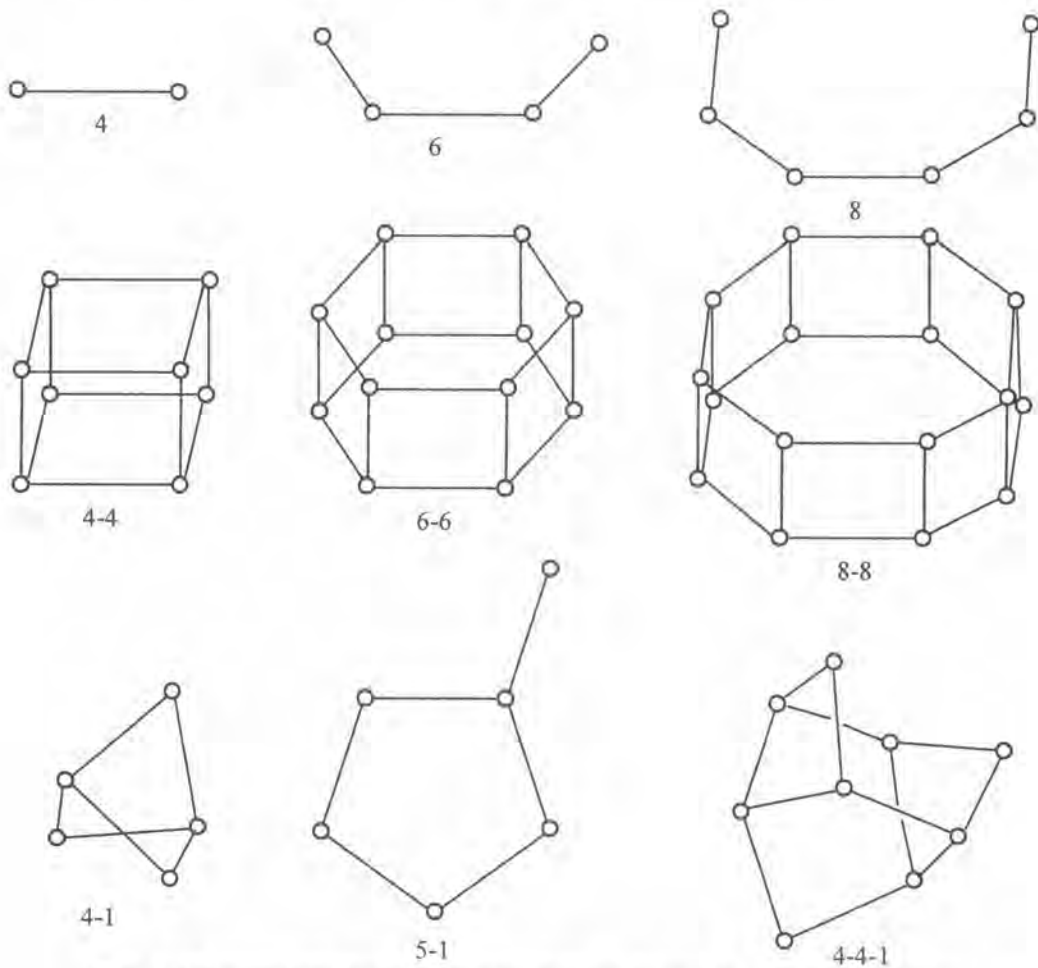


Fig. 2.9 Secondary building units (SBUs) found in zeolite structures.

Table 2.3 Classification of some zeolites and tectosilicates of related topology^[4]

	Idealized unit cell composition	Pore volume (cm ³ as liquid H ₂ O per cm ₃ of crystal)	Suggested designation of topology
Analcime group			
Analcime	Na ₁₆ (Al ₁₆ Si ₃₂ O ₉₆)16H ₂ O	0.18	ANA
Wairkite	Ca ₈ (Al ₁₆ Si ₃₂ O ₉₆)16H ₂ O	0.18	ANA
Leucite (felspathoid)	K ₁₆ (Al ₁₆ Si ₃₂ O ₉₆)	0	ANA
Rb-analcime (felspathoid)	Rb ₁₆ (Al ₁₆ Si ₃₂ O ₉₆)	0	ANA
Pollucite (felspathoid)	Cs ₁₆ (Al ₁₆ Si ₃₂ O ₉₆)	0	ANA
Viseite	Na ₂ Ca ₁₀ (Al ₂₀ P ₁₀ Si ₆ H ₃₆ O ₉₆)16H ₂ O	-	ANA
Keoheite	Zn _{5.5} Ca _{2.5} (Al ₁₆ P ₁₆ H ₄₈ O ₉₆)32H ₂ O	-	ANA
Natrolite group			
Natrolite	Na ₁₆ (Al ₁₆ Si ₂₄ O ₈₀)16H ₂ O	0.21	NAT
Scolecite	Ca ₈ (Al ₁₆ Si ₂₄ O ₈₀)24H ₂ O	0.31	NAT
Mesolite	Na ₁₆ Ca ₁₆ (Al ₄₈ Si ₇₂ O ₂₄₀)64H ₂ O	0.25	NAT
Thomsonite	Na ₄ Ca ₈ (Al ₂₀ Si ₂₀ O ₈₀)24H ₂ O	0.32	THO
Gonnardite	Na ₄ Ca ₂ (Al ₈ Si ₁₂ O ₄₀)14H ₂ O	0.35	THO
Edingtonite	Ba ₂ (Al ₄ Si ₆ O ₂₀)6H ₂ O	0.35	EDI
Metanattrolite	Na ₆ (Al ₁₆ Si ₂₄ O ₈₀)	-	NAT
Heulandite group			
Heulandite	Ca ₄ (Al ₈ Si ₂₈ O ₇₂)24H ₂ O	0.35	HEU
Clinoptilolite	Na ₆ (Al ₆ Si ₃₀ O ₇₂)24H ₂ O	0.34	HEU
Brewsterite	(Sr, Ba, Ca) ₂ (Al ₄ Si ₁₂ O ₃₂)10H ₂ O	0.32	BRE
Stilbite	Na ₂ Ca ₄ (Al ₁₀ Si ₂₆ O ₇₂)32H ₂ O	0.38	STI
Stellerite	Ca ₈ (Al ₁₆ Si ₅₆ O ₁₄₄)56H ₂ O	0.39	STI
Barrerite	(Ca, Mg) ₂ (Na, K) ₁₂ (Al ₁₆ Si ₅₆ O ₁₄₄)52H ₂ O	0.35	STI
Phillipsite group			
Phillipsite	(K, Na) ₅ (Al ₅ Si ₁₁ O ₃₂)10H ₂ O	0.30	PHI
Harmotome	Ba ₂ (Al ₄ Si ₁₂ O ₃₂)12H ₂ O	0.36	PHI
Gismondine	Ca ₄ (Al ₈ Si ₈ O ₃₂)16H ₂ O	0.47	GIS

Table 2.3 (continued)

	Idealized unit cell composition	Pore volume (cm ³ as liquid H ₂ O per cm ³ of crystal)	Suggested designation of topology
Zeolite Na-P	Na ₈ (Al ₈ Si ₈ O ₃₂)16H ₂ O	0.47	GIS
Amicite	K ₄ Na ₄ (Al ₈ Si ₈ O ₃₂)10H ₂ O	0.28	GIS
Garronite	NaCa _{2.5} (Al ₆ Si ₁₀ O ₃₂)14H ₂ O	0.41	GIS
Merlinoite	K ₅ Ca ₂ (Al ₉ Si ₂₃ O ₆₄)24H ₂ O	0.36	MER
Zeolite Li-ABW			
	Li ₄ (Al ₄ Si ₄ O ₁₆)4H ₂ O	0.28	ABW
Mordenite group			
Mordenite	Na ₈ (Al ₈ Si ₄₀ O ₉₆)24H ₂ O	0.26	MOR
Ferrierite	Na _{1.5} Mg ₂ (Al _{5.5} Si _{30.5} O ₇₂)18H ₂ O	0.24	FER
Dachiardite	Na ₅ (Al ₅ Si ₁₉ O ₄₈)12H ₂ O	0.26	DAC
Epistilbite	Ca ₃ (Al ₆ Si ₁₈ O ₄₈)16H ₂ O	0.34	EPI
Bikitaite	Li ₂ (Al ₂ Si ₄ O ₁₂)2H ₂ O	0.20	BIK
Chabazite group			
Chabazite	Ca ₂ (Al ₄ Si ₈ O ₂₄)13H ₂ O	0.48	CHA
Gmelinite	Na ₈ (Al ₈ Si ₁₆ O ₄₈)24H ₂ O	0.43	GME
Erionite	(Ca, Mg, Na ₂ , K ₂) _{4.5} (Al, Si ₂₇ O ₇₂)27H ₂ O	0.36	ERI
Offretite	(K ₂ , Ca, Mg) _{2.5} (Al ₅ Si ₁₃ O ₃₆)15H ₂ O	0.34	OFF
Levynite	Ca ₃ (Al ₆ Si ₁₂ O ₃₆)18H ₂ O	0.42	LEV
Mazzite	(Na ₂ , K ₂ , Ca, Mg) ₅ (Al ₁₀ Si ₂₆ O ₇₂)28H ₂ O	0.37	MAZ
(Zeolite Ω)			
Zeolite L	K ₆ Na ₃ (Al ₉ Si ₂₇ O ₇₂)21H ₂ O	0.28	LTL
Sodalite hydrate			
	Na ₆ (Al ₆ Si ₆ O ₂₄)8H ₂ O	0.34	SOD
Cancrinite hydrate			
	Na ₆ (Al ₆ Si ₆ O ₂₄)8H ₂ O	0.34	CAN
Zeolite Losod	Na ₁₂ (Al ₁₂ Si ₁₂ O ₄₈)19H ₂ O	0.37	LOS
Faujasite group			
Faujasite (zeolites X and Y)			
	Na ₁₂ Ca ₁₂ Mg ₁₁ (Al ₅₉ Si ₁₃₃ O ₃₈₄)26H ₂ O	0.53	FAU
Zeolite ZSM-3			
	{(Li, Na) ₂ (Al ₂ Si _{3.2} O _{8.4}) _m }	0.53	MTH

Table 2.3 (continued)

	Idealized unit cell composition	Pore volume (cm ³ as liquid H ₂ O per cm ₃ of crystal)	Suggested designation of topology
Paulingite	(K ₂ , Na ₂ , Ca, Ba) ₇₆ (Al ₁₅₂ Si ₅₂₅ O ₁₃₅₄)700H ₂ O	0.48	PAU
Zeolite A	Na ₁₂ (Al ₁₂ Si ₁₂ O ₄₈)27H ₂ O (pseudo cell)	0.47	LTA
Zeolite RHO	(Na, Cs) ₁₂ (Al ₁₂ Si ₃₆ O ₉₆)46H ₂ O	0.41	RHO
Zeolite ZK-5	Na ₃₀ (Al ₃₀ Si ₆₆ O ₁₉₂)98H ₂ O	0.45	KFI
Laumontite group			
Laumontite	Ca ₄ (Al ₈ Si ₁₆ O ₄₈)16H ₂ O	0.35	LAU
Yugawaralite	Ca ₄ (Al ₈ Si ₂₀ O ₅₆)16H ₂ O	0.30	YUG
Pentasil group			
Zeolite ZSM-5	Na _n (Al _n Si _{96-n} O ₁₉₂)16H ₂ O, with n typically about 3	0.32	MFI
Zeolite ZSM-11		0.32	MEL
Clathrate group			
Melanophlogite	(Si ₄₆ O ₉₂)	-	MEP
Zeolite ZSM-39	(Na, TMA, TEA) _{0.4} (Al _{0.4} Si _{135.6} O ₂₇₂)nH ₂ O	-	MTN

B. Properties of zeolite^[3, 51, 52]

1. Adsorption

The most fundamental consideration regarding the adsorption of chemical species by zeolites is molecular sieving. Species with a kinetic diameter which makes them too large to pass through a zeolite pore are effectively "sieved".

Zeolite molecular sieves are selective, high-capacity adsorbents because of their high intracrystalline surface area and strong interactions with adsorbates. Molecules of different size generally have different diffusion properties in the same molecular sieve.

Molecules are separated on the basis of size and structure relative to the size and geometry of the apertures of the sieve. Molecular sieves adsorb molecules, in particular those with a permanent dipole moments, and exhibit other interactions not found in other sorbents. Different polar molecules have a different interaction with the molecular sieve framework, and may thus be separated by a particular molecular sieve. This is one of the major uses of zeolites. An example is the separation of N_2 and O_2 in the air on zeolite A, by exploiting different polarities of the two molecules.

The ring sizes of zeolite molecular sieve may be determined by sorption of molecules of different size. Water and nitrogen are two of the smallest molecules which can easily penetrate almost the entire structures. These two molecules are normally used to determine the crystallinity of molecular sieves by comparing the adsorption volume with that of a standard sample.

2. Thermal stability

The resistance to collapse at elevated temperatures was one of the first recognized manifestations of zeolite stability. The discovery that these materials could be heated past the point of dehydration without collapse attracted widespread attention.

The geometry of the crystalline network is undoubtedly a major factor in stability. However, the quantitative relationship has not been determined and researchers are still unable to predict the stability of a given structure. Even empirical correlations between stability and structure are difficult because other factors make simultaneous contributions. Intuitively, the more dense structures might have a higher degree of stability because of their thicker walls between pores or channels. In general, there is a relation between the silica-to-alumina ratio of a zeolite and its thermal stability; the more siliceous zeolites tend to be more stable.

3. Chemical stability

Chemical stability of zeolites is usually considered from their applications. One of the greatest limitations in the application of zeolites is acid resistance. The

aluminosilicate zeolites have limited stability in acid media because of the solubility of aluminum away from the structure. Hydrated alumina becomes appreciably soluble at a pH of about 4. In the presence of hydrated silica, the solubility of aluminum is suppressed to a slightly lower pH. The zeolites are chemically similar in nature to other aluminosilicate minerals and to the hydrated amorphous silica-alumina. They are especially susceptible to acid attack because, in most cases, their aluminum is essentially all surface aluminum and receives little or no protection by being buried or inaccessible. Some clays, for example, resist acid leaching of the aluminum because it is largely located between silicate layers and therefore inaccessible to the aqueous phase. Heat treatment delaminates the layer structure, making the aluminum susceptible to acid extraction. Zeolites, by their nature, are extremely open structures and their aluminum is consequently subject to acid attack.

There is very little quantitative data in the literature concerning the stability of zeolites to acid attack. Nevertheless, It can be distinguished three categories of behaviors concerning their acid stability:

(i) Those that cannot be put into the acid form without collapse of the crystalline framework.

(ii) Those that can be put into the acid form by a conventional ion-exchange process with an acidic solution. (There is undoubtedly some removal of aluminum involved, the amount being dependent on the acid used, its concentration, etc.)

(iii) Those that can be conveniently put into the acid form only by an indirect method wherein an ion exchange is performed with some ion such as ammonium, which upon subsequent heating will decompose, leaving the zeolite in the acid form.

4. Ion exchange

One important property of zeolites is the ability to exchange cations. This is the trading of one charged ion for another on the crystal. One measure of this property is the cation exchange capacity (CEC). Zeolites have high CEC, arising during the formation their framework structures from the substitution of aluminum atom for silicon atom. They

usually contain cation (e.g. Na^+ , K^+ or NH_4^+) after the synthesis. For example, by exposing a sodium containing zeolite to a solution containing other cations, the sodium ions can be exchanged by these other cations provide

5. Acidity

When an aluminum atom substitutes a silicon atom, the +III valence of aluminum introduces a net negative charge in the framework. Cations are then required to preserve neutrality. Not only this presence of cations allows zeolite crystals to be used in ion-exchange processes but it creates an acid site if protons act as counterions. However, it would be too simple to represent acid sites in zeolite by a simple proton like classical homogeneous acids. Fig.2.10 shows a typical zeolite acid site. It consists of a hydroxyl group bridging a silicon atom and an aluminum atom corresponding to a strong Brønsted site and oxobridges exhibiting Lewis base properties. The acidity of zeolite is very strong, about 1000 stronger than that of amorphous aluminosilicates. In catalytic applications, high-silica zeolite is preferred because of the thermal stability of their framework (crucial for regeneration cycles) and high dispersion of acid sites. Moreover, low aluminum content ensures high acidity for each proton.

The reactivity and the selectivity of molecular sieve zeolites as catalyst are determined by active sites. Classical Brønsted and Lewis acid models of acidity have been used to classify the active sites on zeolites. Brønsted acidity is proton-donor acidity; this occurs in the zeolites when the cations balancing the framework anionic charge are protons (H^+). Lewis acidity is electron acceptor acidity; a trigonally coordinated aluminum atom, for example, is electron-deficient and can accept an electron pair, and thus behaves as a Lewis acid. The protons which balance the negative charge of the zeolites framework are not strongly bound to the framework and are able to move within the pore and react with molecules which penetrate into the zeolite pore system.

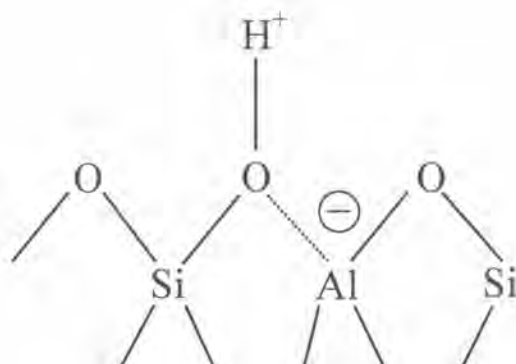


Fig. 2.10 Active site in zeolite.

To produce the zeolite acid catalyst, it is necessary to replace the cations present in the freshly synthesized material with protons. This may at first appear simple; however there are several difficulties associated with such an exchange:

(i) Most of the recent high-silica zeolites are synthesized in the presence of large organic quaternary amine cations that incorporate and remain within the channel system. After crystallization is complete, they must be removed before ion exchange is possible.

(ii) Several exchanges may be necessary, as direct ion exchange of a proton into the zeolite will not be 100% successful upon the first exchange.

(iii) For direct proton exchange, if an acid is contacted with the zeolite structure for extended periods of time, dealumination (removal of framework aluminum) is observed.

6. Shape selectivity

Shape selectivity plays a very important role in molecular sieve catalysis. Highly crystalline and regular channel structures are among the principal features that molecular sieves used as catalysts offer over other materials. Apart from those acidic properties, zeolite is shape selective regarding molecular adsorption. This is due to their pore system that can be one, two or three-dimensional and contain pores of different size which are in the order of molecular dimensions (from about 0.3-1.2 nm). The void dimensionality and

very high internal surface area ($>500 \text{ m}^2/\text{g}$) are responsible for catalytic shape selectivity of zeolite. Derouane et al. proposed in the 1980s the so-called confinement effect in order to describe interactions of adsorbed molecules within the curved surface of channels and cages of zeolite. It is obvious that sorbate-framework interactions and the local framework topology around the active site largely influence the reactivity of molecules.

Shape selectivity was first observed by Weisz and Frillette in 1960. Since then this phenomenon has been thoroughly documented in literature. Reactions within zeolite can be inhibited if there is no matching between certain molecules and a sterically confined environment allowing conversion of reactants. The unique one, two or three-dimensional pore system of zeolite enables shape selective catalysis. There is a consensus on the different mechanisms (Fig. 2.11) of molecular shape selectivity in zeolite technology:

a) Reactant selectivity

This occurs when some molecules preferentially enter zeolite pore mouth whereas others are rejected because they are too large with respect to the pore openings. Once a reactant has adsorbed in the zeolite channels, it must diffuse towards active sites where reactions can occur. This is where the two following selectivity phenomena can occur.

b) Product selectivity

This occurs when some reaction products or intermediates formed within the pores are too bulky to diffuse out. They are either converted to smaller molecules or deactivate the catalyst by blocking of the pores. After reaction has occurred, products must diffuse away from the micropores which results in a kind of molecular traffic control.

c) Transition state selectivity

The distinction between transition state selectivity and product selectivity is not always obvious. It takes place when the transition state cannot be accommodated in the space available in the intra crystalline volume. A way to differentiate product and

transition state selectivity is to vary the crystal size because only product selectivity depends on crystal size, whereas transition state shape selectivity does not.

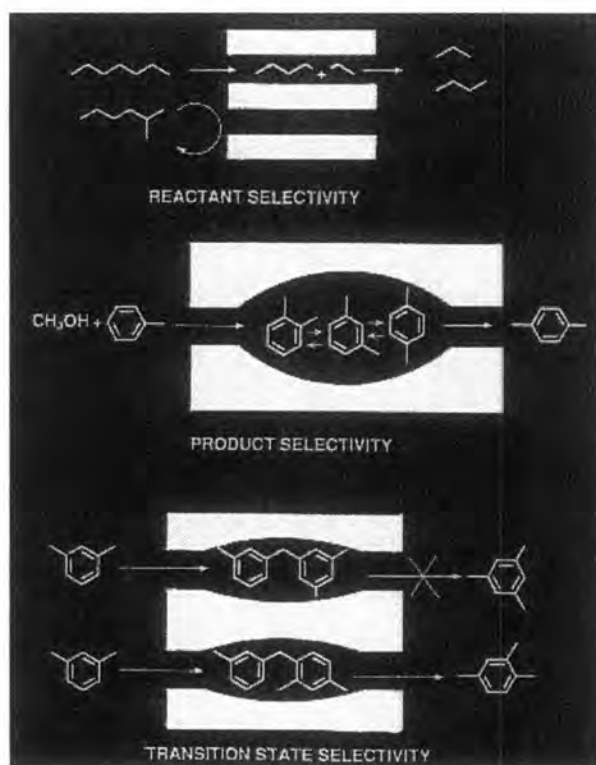


Fig. 2.11 Diagram depicting the three types of selectivity: reactant, product and transition-state shape selectivity.

C. Synthesis of zeolite

The synthesis of zeolites is carried out under hydrothermal conditions. An aluminate solution and a silicate solution are mixed together in an alkaline medium to form milky gel or in some instances, clear solutions. Various cations or anions can be added to the synthesis mixture. Synthesis proceeds at elevated temperatures (60-200 °C) where crystals form through a nucleation step. A schematic representation of zeolite formation process is given in Fig. 2.12.

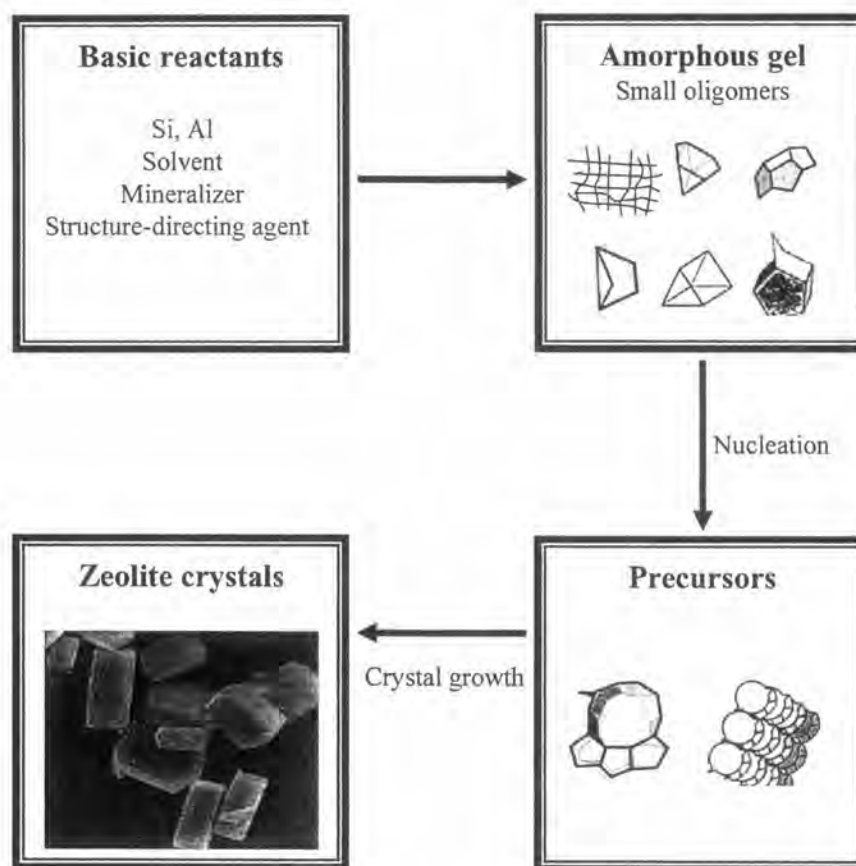


Fig. 2.12 Simplified zeolite synthesis scheme^[51].

The following sections give a general overview on the parameters governing zeolite synthesis.

1. Molar composition

Although this is not an independent parameter, every zeolite has a specific molar composition range often represented graphically in a ternary compositional phase diagram (Na_2O , Al_2O_3 and SiO_2). On the other hand, each structure will also impose constraints on the amount of Al it can incorporate. High-silica molecular sieves such ZSM-5 can be synthesized over a wide range of Si/Al ratios (Si/Al from 7 to infinity)

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the gel places a constraint on the framework composition of the zeolite produced. With the exception of the aluminum-rich zeolite NaA, zeolites

normally incorporate all of the aluminum present in the reaction mixture into their framework structure, leaving varying amounts of silica or silicate in solution, according to other factors such as the hydroxide ion concentration and the presence of various inorganic and organic cations in the reaction mixture. For catalytic applications such as catalytic cracking and isomerization, zeolites become more useful as the silica/alumina ratio is increased. Acid resistance and thermal stability, two properties critical for the success of a zeolite as catalyst for these applications, are both improved with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$. On the other hand, for many adsorption and ion exchange processes, decreasing the silica/alumina ratio will increase the cation content, producing an improved hydrophilic adsorbent or ion exchange material. The effects of changing the silica content of a zeolite are summarized in Table 2.4.

Table 2.4 Effect of changing $\text{SiO}_2/\text{Al}_2\text{O}_3$ on the physical properties of the zeolite

Increasing silica/alumina in a zeolite:

- Increases acid resistance
- Increases thermal stability
- Increases hydrophobicity
- Decreases affinity for polar adsorbates
- Decreases cation content

Decreasing silica/alumina in a zeolite:

- Increases hydrophilicity
 - Increases cation exchange properties
-

Ideally the desired $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of a zeolite chosen for a specific application should be obtainable through adjusting that ratio in the synthesis mixture. Unfortunately, changing the ratio of silica to alumina in the reaction mixture to produce the desired aluminum content not only will cause a change in the aluminum concentration in the zeolite structure, but it may also result in a change in the final structure obtained.

In addition to the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, various other factors must be included in the composition of the reaction mixture, with structure directing their influence in the zeolite

synthesis recipe. These factors include: OH^- concentration, cations (both organic and inorganic), anions other than OH^- and water concentration.

2. Mineralizer

A mineralizer is a species which enables the formation of a more stable solid phase from a less stable solid phase via dissolution and crystallization. Supersaturation can be reached by dissolution and these soluble species are then available for nucleation and crystal growth. In most cases, hydroxyl ions act as mineralizing agents. Indeed, OH^- increases the solubility of silica by depolymerizing amorphous silica particles. Oligomeric species are then present in the solution. Condensation of specific aluminosilicate species, facilitated by the presence of OH^- , occurs and leads to the appearance of the first crystals. In general high pH values increase crystal growth rates and shorten the nucleation period. Hydroxyl ion concentration can also influence crystal morphology, crystal yield and final zeolite structure. A summary of the role hydroxide ion have in the crystallization of zeolite structures is given in Table 2.5.

Table 2.5 Role of hydroxide ion in crystallization of zeolite structures

-
- Functions as structure director through control of the degree of polymerization of silicates in solution.
 - Modifies nucleation time by influencing transport of silicates from the solid phase to solution.
 - Enhances crystal growth by influencing transport between the solution phase and the growing crystal.
 - Control phase purity through influencing the rate of transport of silicate species from one crystalline phase to another.
-

Fluoride ions have been used as mineralizers. Silicalite-1 was the first zeolite synthesized from acidic F^- medium. Fluoride anions act similarly to hydroxyl ions without contributing directly to the pH of the system. Nucleation and crystal growth rates are generally slowed down resulting in large and high quality crystals. The fluoride ion

synthesis route has mostly been applied in the area of aluminophosphates mainly because it has led to the discovery of novel aluminophosphates and isomorphously substituted versions that cannot be obtained at high pH.

3. Water

The water content of the starting mixture also plays an important role in the direction of structure for certain zeolite. Water has been proposed to interact strongly, in some cases, with the cations present in solution, thus itself becoming part of the “template” for structure directing. Transport properties within the gel and the viscosity of the reacting gel change with changing water concentration.

In mordenite synthesis, for example, the production of large-port mordenite depended strongly on water content. The H_2O/Na_2O ratio in the starting mixture is inversely proportional to the alkalinity. At constant temperature, time and silica/alumina, the trends in product formation were in the direction analcime/phillipsite to mordenite to amorphous phase, with an increase in H_2O/Na_2O . A higher H_2O/Na_2O in the initial mixture corresponds to lower concentrations of the various components (aluminum and silicon) in the liquid phase. This in turn results in the formation of the less stable phase. Conversely, lower ratios of H_2O/Na_2O in the starting mixture correspond to higher concentration of the various components in the liquid phase, resulting in the formation of more stable zeolite phases. Even though the presence of organic species in solution exerts a strong influence on the structure crystallized, water too can “tip the balance” of which structure crystallizes.

4. Temperature

Temperature influenced several factors in zeolite synthesis; it can alter the zeolite phase as well as change the induction period before the start of crystallization. This induction period decreases with increasing temperature. Domine and Quobex reported that at a fixed pH of 12.6 the induction period in the formation of mordenite varied from 1 h at 350 °C to 4 weeks at 100 °C and 2 days at 200 °C. Also, for any mixture as the temperature increases, the rate of crystallization increases. As the temperature is changed,

conditions may favor formation of other phases. For example, in the synthesis of zeolite mordenite, the sequence of formation of the products with an increase in temperature was in the direction: amorphous to mordenite to analcime. This shift in temperature of synthesis can be explained by the following mechanism: The concentration of the components (aluminate and silicate in the liquid phase of the mixture, generally gel) appears as the main controlling factor for the formation of a zeolite. As the temperature increases, the solubilities of the aluminate and silicate species increase, causing a shift in the concentration of the liquid phase. This results in the formation of analcime in place of mordenite. Hence, if mordenite must be crystallized at higher temperatures, the starting mixture would require relatively higher silica or lower caustic content, which means reduction of the alkalinity in order to counter the effect of changing the crystallization temperature.

5. Silica and alumina sources

Nucleation and growth kinetics can depend on the dissolution of the solid reagents and formation of aluminosilicates precursors. Kühl found that crystallization of some structures was dependent on the degree of prepolymerization of the silica source. Mintova and Valtchev recently investigated the colloidal distribution of silicalite-1 synthesis mixtures containing different silica sources. Impurities in silica or alumina sources are likely to influence crystallization kinetics and framework composition. There are a variety of silica sources available and these are summarized in Table 2.6. These materials vary in their cost, reactivity, purity and their ease of handling.

Table 2.6 Examples of typical silica sources^[11]

Silica source	Formula	Comments
Sodium water glass	$0.3\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 7\text{H}_2\text{O}$	Cheap. Low levels of Al
Precipitated silica	SiO_2	Cheap. Contains NaCl and low levels of Al
Colloidal silica	SiO_2	More expensive. Usually available with SiO_2 contents ~30-40% w/w. Stabilized with Na or NH_4
Fumed silica	SiO_2	More expensive. Very pure. Very low levels of Al and Cl
TEOS	$\text{Si}(\text{OC}_2\text{H}_5)_4$	More expensive. Very pure. Must be hydrolyzed generating an aqueous ethanol solution

6. Structure-directing agents

Structure direction occurs when inorganic or organic molecules are used to direct the crystallization towards a specific zeolite structure. Structure-directing agents, currently called templates, are generally: (i) Charged molecules which are mostly cations. Inorganic cations such as Na^+ , K^+ , Li^+ and Ca^{2+} are frequently used. Organic molecules that are used are usually tetraalkylammonium, dialkyl and trialkyl amines or phosphonium compounds. (ii) Neutral molecules. Water actually plays an important role in the structure direction encountered in zeolite synthesis. Water molecules act as void fillers in order to stabilize the porous oxide framework. Interactions of water molecules with cations are part of the template effect and therefore are of crucial importance. Other molecules include amines, ethers or alcohols. (iii) Ionic pairs: Salts (NaCl , KCl , KBr) are occluded into the zeolite framework as guest molecules, stabilizing the zeolite framework.

D. Zeolite applications

Zeolite has been widely used for the following main applications:

1. Adsorption

Zeolite (in particular, zeolite A developed by Union Carbide) has enjoyed widespread commercial application of its molecular sieving properties. It is used to adsorb a variety of materials including application in drying, purification and separation. Zeolite A is especially attractive in this application because its effective pore size can readily be varied by ion exchange. It can behave as a porous crystal having pores of about 3, 4 or 5 Å, depending respectively on whether it is largely in the K, Na or Ca ion-exchanged form.

2. Catalysis

More zeolites are currently used in catalysis than in any other application. Cracking catalysts for converting petroleum into lighter products including gasoline, fuel oil and petrochemical feeds have provided the major market for these materials. In many chemical reactions, zeolite is proved to be excellent catalysts when compared with other known catalytic materials. The successful commercial application of zeolite has closely corresponded to understanding and controlling the factors that affect their stability. Many commercially important applications require a catalyst to endure extremely harsh environments. High temperatures in the presence of steam, for example, are often encountered in the regeneration of catalysts where carbonaceous materials formed as a by-product of the reaction are burned off.

3. Ion exchange

Zeolite found early application in the removal of undesirable ions from water, i.e., for water softening. This was accomplished by ion exchange or an exchange of ions between the aqueous solution and the zeolite phase. Kunin lists several essential features of a satisfactory exchanger. They include the following:

- The functional groups must be present in reasonably large numbers per unit weight or volume.
- The functional groups must be accessible to ions in solution.

- The ion exchange materials must be physically and chemically durable over a wide range of conditions.

Deterioration of the ability of zeolite to function satisfactorily as an ion exchanger is most often observed as a loss in the exchange capacity. This may arise from several causes, including fouling of the porous structure, a collapse of the porous structure, mechanical loss in attrition, or the destruction of the exchange site by an irreversible exchange or by acid attack.

In summary, synthetic zeolite has been grown to an estimate \$ 1.6-1.7 billion industry. Detergents represent the largest volume. LTA-type zeolites substitute phosphate compounds in the water softening process in laundry. The largest market value for zeolite is in refinery catalysis. FCC (fluid Catalytic Cracking) catalysts account for more than 95% of zeolite catalyst consumption and consist of various forms of zeolite Y. MFI-type zeolite is the second most used catalyst, primarily because they are added to FCC catalysts for octane number enhancement. Zeolite is also employed in the drying and purification of natural gas, separation of paraffins and desulfurization processes. Despite being in a relatively early stage of development, zeolite is also used in fine chemicals production such as oxidation and acylation. The main applications of zeolite are summarized in Table 2.7.

Zeolite science appears to be a mature science and still a very dynamic field. Discoveries of new zeolites continuously open new areas of development. New trends at the beginning of this century include environmental applications such as De-NO_x catalysis and hydrocarbon storage in vehicles powered with diesel or gasoline engines, and biopharmaceutical applications. Zeolite can also be used in the nuclear industry for radioactive waste storage. Applications of zeolite material science still play an important role in many areas of technology.

Table 2.7 Main commercial applications involving zeolites

Process	Catalyst	Products
Catalytic cracking	Re-Y, US-Y, ZSM-5	Gasoline, fuels
Hydrocracking	Y, Mordenite + Mo, W, Ni	Kerosene, diesel, Benzene
Alkylation of aromatics	ZSM-5, Mordenite	<i>p</i> -xylene, ethyl-benzene, styrene
Hydroisomerization	Mordenite + Pt, Pd	<i>i</i> -pentane, <i>i</i> -hexane
Xylene isomerization	ZSM-5	<i>p</i> -xylene
Catalytic dewaxing	Mordenite, ZSM-5 + Ni, noble metals	Improvement of cold flow properties
Transalkylation	Mordenite	Xylenes, cumene
MTBE	ZSM-5	Aromatics, paraffins
MTG	Ga-ZSM-5	Aromatics

E. ZSM-5 zeolite

1. Structure of ZSM-5

In 1972, Argauer and Landolt from Mobil Oil Corporation reported the first patent on the synthesis of a pentasil aluminosilicate zeolite, termed as ZSM-5 (Zeolite Socony Mobil #5)^[53]. ZSM-5 is a highly siliceous zeolite with MFI structure (Fig. 2.6) which is constructed using five member ring building units. The combination of these building units results in a framework containing two perpendicular intersection channel systems; one is sinusoidal and the other is straight. The sinusoidal system runs parallel to (001) and has near circular pore openings with free dimensions varying from 0.54 nm to 0.56 nm. The straight system (Fig. 2.13) runs parallel to (010) and has an elliptical shape with dimensions ranging from 0.51 nm to 0.54 nm. The pore openings are elliptical 10-member rings. There are 12 unique T atom sites in ZSM-5. This structure is successfully described in the orthorhombic space group Pnma.

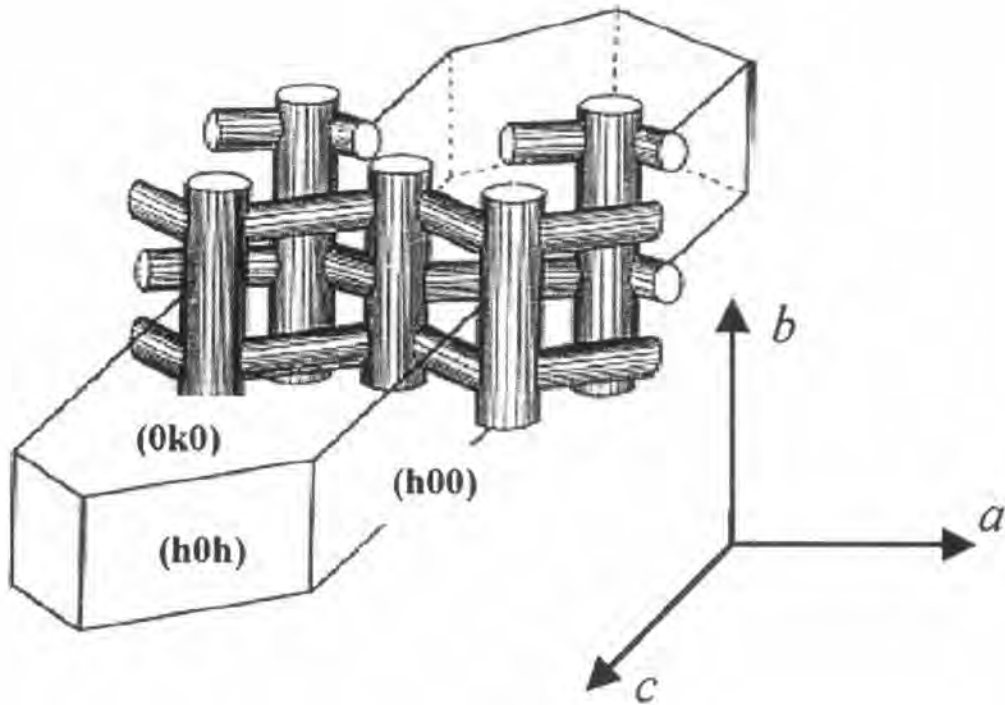


Fig. 2.13 A drawing visualizing a MFI crystal and orientation of its pore structure^[54].

2. Properties and applications

ZSM-5 zeolite has been widely used as catalysts and sorbents in several industrial applications, especially petroleum and petrochemical industry, due to its unique shape selectivity, solid acidity, ion exchangeability, pore size, thermal stability and structural network. The largest utilization of ZSM-5 has been in the fluidized catalytic cracking (FCC) process and recently with some modifications in the area of production of fine chemicals. In the FCC process, a wide range of heavier petroleum fractions are converted to lighter boiling gasoline and light fuel oil. The major byproducts of the process are liquefied petroleum gas (LPG), fuel gas, and petroleum coke. The current major applications have many uses of commercial ZSM-5 (Fig. 2.14) including:

- Fluid catalytic cracking (FCC)-octane enhancing.
- Xylene isomerization.
- Dewaxing.
- Methanol to gasoline conversion.

- Ethylbenzene synthesis.
- *p*-Methylstyrene synthesis.

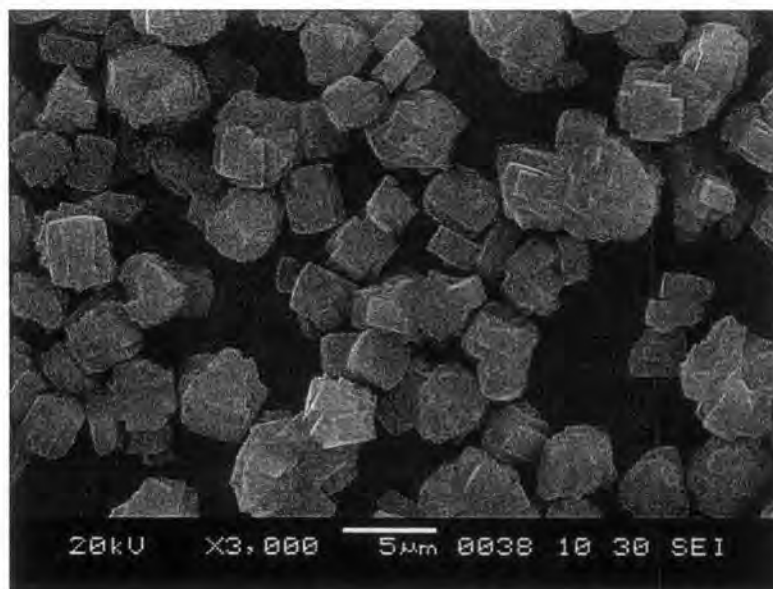


Fig. 2.14 Representative SEM micrograph of commercial ZSM-5 zeolite.
(H-ZSM-5, HSZ-89 OHOA).

3. Synthesis

Generally ZSM-5 is synthesized from hydrogels containing a structure directing agent and precursors of silicon and aluminum species by hydrothermal method under autogenous pressure at temperature above 100 °C^[55-61]. In the ZSM-5 system, crystallization occurs over a wide range of silica/alumina from 15 to infinity. Unlike the natural zeolites and other synthetic materials such as types A, X and Y, this structure crystallizes readily without the addition of any aluminum-containing component in the reaction mixture. The high-silica end member or pure silica polymorph with silica/alumina ratios from 250 to infinity, silicalite, contains aluminum only as structural aluminum arising from aluminum impurities found in the other components of the initial

reaction mixture. Attempt to prepare ZSM-5 at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios less than 15 result in the crystallization of a mordenite or other less silica-rich phase.

The pathway of the crystallization process as well as the morphology and singular properties (crystal size and distribution) of MFI-type zeolite are influenced by different variables: the silicon and aluminum source, the aluminum content, the template/silicon ratio, the nature of cations present in the synthesis medium, the alkalinity, the temperature of crystallization, the presence of seeds, the water content, etc. These variables affect the physicochemical properties of ZSM-5 such as morphology, crystal size, surface area, acidity and Si/Al in the zeolite structure.

a) Effect of organic template

ZSM-5 is a very versatile zeolite since it can be made from various organic or inorganic agents over a wide range of synthesis conditions. ZSM-5 was first synthesized using expensive TPAOH (tetrapropylammonium hydroxide) solution. Later, the same structure was synthesized using different organic templates.

Tetrapropylammonium (TPA) has been regarded as the most efficient template in high-silica ZSM-5 synthesis, thereby appearing as a true example of structure direction. It indeed enhances nucleation rate and accelerates crystallization. Moreover TPA molecules are located at the channel intersections with their propyl arms extending into linear and zig-zag channels. They are tightly encapsulated so that calcination is required to obtain their removal. This tight entrapment suggests that TPA molecules are actively involved in the nucleation period and crystal growth. Burkett and Davis, using ^1H - ^{29}Si CP, investigated relationships between TPA and silicate species.

Evidences of close interactions between TPA cations and silicates species have been observed well before the formation of long-range crystalline structure. They proposed that the key steps for structure direction were the formation of inorganic-organic composite entities which may be the precursors of units participating in nucleation and crystal growth. No such interactions were observed when a molecule lacking of structure-directing properties (i.e. TMA) was used, suggesting that these

intermolecular contacts are specific. At the same time, Dokter et al. have observed primary silica particles in the range of 1-20 nm by means of small-angle X-ray/neutron scattering (SAXS/SANS). They suggested that these colloidal particles underwent several aggregation and densification steps leading to the formation of the first crystals.

De Moor et al., using a combination of in situ SAXS, USAXS and WAXS (ultra small wide-angle X-ray scattering), recently found three particle populations during TPA-mediated silicalite-1 crystallization. Primary units with a size of 2.8 nm, their consumption monitored through the whole course of crystallization. By varying the alkalinity, it was found that 2.8 nm particles were always present unlike their aggregates of which the formation depends on the Si/OH ratio. However, the formation of the aggregates appeared to be an essential step in the nucleation process since it enhances the nucleation rate. It was suggested that crystal growth probably occurs via the addition of the 2.8 nm primary units to the growing crystals. Moreover, the same size for primary units was observed using three other structure-directing agents (a dimer of TPA, a trimer of TPA and trimethylene-bis (N-hexyl, N-methyl-piperidium)). Nanoscale precursors were also found in the crystallization of the other zeolites such as Si-BEA, Si-MTW from gelling systems. A mechanism was then proposed for organic-mediated zeolite synthesis and is depicted in Fig. 2.15

Moreover, ZSM-5 has also been reported to form in the absence of the organic template. In 1972, it was originally prepared in the presence of the organic TPA cation with a range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ claimed between 15 and 100. This range over which the structure crystallizes was further extended to include the pure silica polymorph, silicalite. ZSM-5 was shown to crystallize from an organic-template-free or exclusively inorganic system. The main thrust of this research has involved a search for preparing this useful zeolite at a lower cost (the organic amine contributing the major expense in a commercial process) and a lower toxicity (many of the organic amine bases that had been used to crystallize the structure being highly toxic). But on another level, the ability to crystallize this zeolite without the need for an organic species to be present raises a question about the structure-directing role of the organic cations in assisting the crystallization of this structure so it is evidence for the ability of the organic additive to extend the range of

$\text{SiO}_2/\text{Al}_2\text{O}_3$ for a given zeolite structure. Successful preparation of this structure in the absence of the organic amine cation is limited to a narrow range of aluminum concentration ($\text{SiO}_2/\text{Al}_2\text{O}_3$ between 60 and 100). At higher silica/alumina, nonzeolitic phases precipitate, including kenyaite or magadite. On the other hand, at higher concentrations of aluminum, crystallization of the mordenite phase is preferred. A secondary contributor to template-free zeolite growth is the caustic concentration. Here too the range where the ZSM-5 structure crystallizes is limited. Crystallization of the ZSM-5 structure in the template-free system has been reported around a $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio of 0.01 to 0.20.

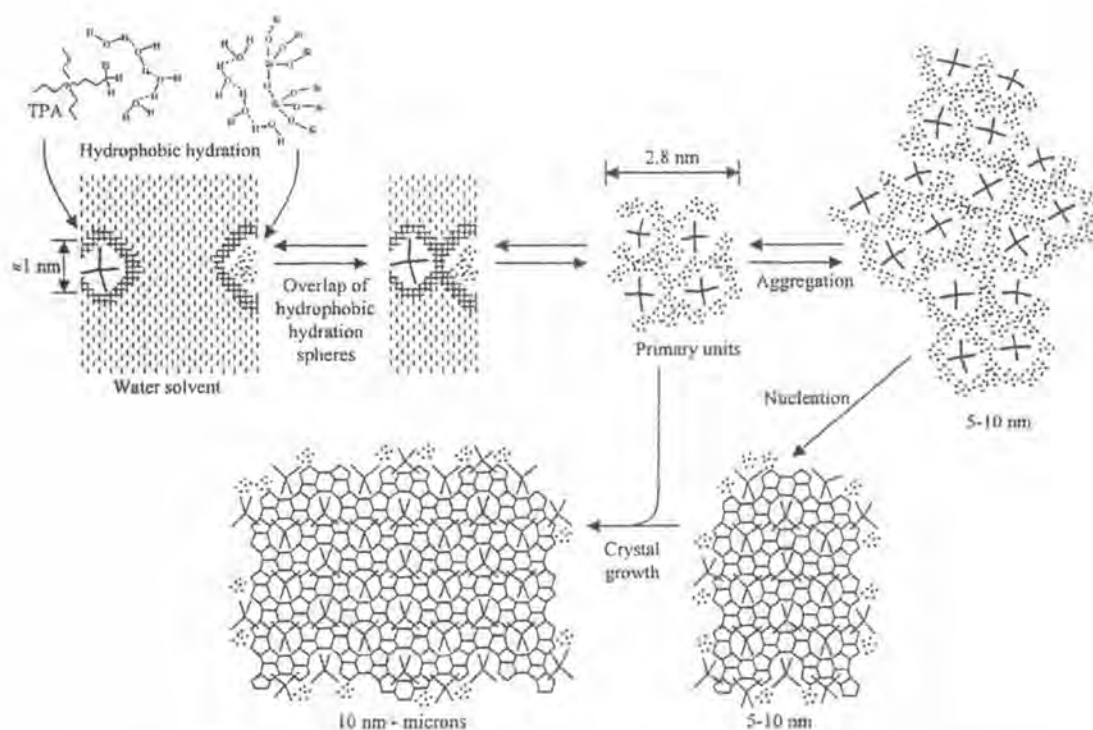


Fig. 2.15 Scheme for the crystallization mechanism of Si-TPA-MFI^[26].

The contribution of seeds or trace amounts of organic reagents has been examined in their ability to promote crystallization of this structure within the "template-free" concentration range. Although both appear to modify crystallization- seeding accelerated crystallization, and the addition of an organic such as acetone increased the percent crystallized-they do not appear to be critical in producing the desired ZSM-5 structure. TPA present during growth does improve the quality of the resulting crystals, in addition to its role in directing crystallization toward that structure over an extremely an extremely wide range of silica/alumina.

The presence of the organic component is also found to stabilize the ZSM-5 phase in the mother liquor. Without the organic amine, a slow recrystallization to quartz can be observed after 24 hours. This, however, can be suppressed by changing the thermal reaction conditions. Temperatures below 190 °C will slow the recrystallization. The ability of ZSM-5 structure to crystallize in the absence of organic additives in the initial gel gives little indication of the true structure-directing crystallization of this particular structure. It does indicate the influence the presence of the organic in the synthesis mixture has over the other reaction parameters, especially in extending the range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ at which this structure can crystallize. This suggests possibilities of the other roles that these organic species may play in zeolite crystallization, beyond the role of "template" in zeolite crystallization.

b) Effect of silica and alumina content

The addition of aluminum to the crystallization mixture was not required for the formation of the ZSM-5 structure. In fact, the crystallization rate for the formation of this structure increases as the aluminum content decreases, with a rapid increase in rate above a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 100. This relationship between crystallization rate and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for ZSM-5 is in direct contrast to the behavior of other zeolite systems known at the time, where high aluminum contents in the gel led to increasing crystallization rates. Generally, the presence of high concentrations of silica in the crystallization mixture, known to increase the viscosity of the solution, slows crystal growth. In some cases the favored crystallization of the high-silica (silicalite) form can lead to inhomogeneities in the

resulting product, with mixtures of silicalite crystals and aluminum-containing crystals occurring. After crystallization is complete, analysis of the as-synthesized ZSM-5 shows that this structure will, in general, incorporate into its framework the aluminum present in the initial mixture.

c) Effect of alkalinity

Besides the dependence of the crystallization rate on the amount of aluminum present in the starting mixture, the alkalinity of the mixture plays a dominant role in ZSM-5 synthesis, affecting the size of the crystalline material produced. The high silica content of this structure makes this material particularly sensitive to solubilizing in highly alkaline media. In high hydroxide environments, crystal growth and dissolution compete and smaller crystals result. At low hydroxide concentrations, large crystals have been found to form. Larger crystals have also been encouraged to form through the addition of tetramethylammonium cations or oxyethylacetamide.

TiO₂ photocatalysis

A. Crystal structure of TiO₂

Titanium dioxide (TiO₂) or titania mainly exists in three crystalline polymorphs, namely, anatase, rutile and brookite^[62-65]. Each phase exhibits different physical properties as shown in Table 2.8. The stable form of rutile tends to be more stable at high temperatures, whereas anatase and brookite tend to be more stable at lower temperatures and are readily transformed to rutile when heated. Moreover, the size dependence of the stability of various TiO₂ phases has recently been reported. Rutile is the most stable phase for particles above 35 nm in size. Anatase is the most stable phase for nanoparticles below 11 nm. Brookite has been found to be the most stable for nanoparticles in the 11-35 nm range^[66], although the Grtätzel group found that anatase was the only phase for their nanocrystalline samples. These have different activities for photocatalytic reaction, but the precise reasons for differing activities have not been elucidated in detail.

Anatase and rutile have tetragonal structure, whereas brookite is orthorhombic. All three crystalline structures consist of deformed TiO₆ octahedra connected differently

by corners and edges^[67]. In rutile two octahedra edges are shared to form linear chains along the [001] direction and the TiO₆ chains are linked to each other through corner-shared bondings. In anatase, each octahedron shares four edges with other four octahedra, resulting in a zigzag structure. In brookite, each octahedron shares three edges and the octahedral arrangement produces a crystalline structure with tunnels along the c-axis. The different crystal structures of TiO₂ are shown in Fig. 2.16.

Table 2.8 Physical properties of rutile, anatase and brookite^[62, 63, 68]

Properties	Rutile	Anatase	Brookite
Molecular weight	79.89	79.89	79.89
Crystal system	Tetragonal	Tetragonal	Orthorhombic
Point group	4/mmm	4/mmm	mmm
Space group	P4 ₂ /mnm	I4 ₁ /amd	Pbca
Unit cell			
a (Å)	4.5845	3.7842	9.1840
b (Å)			5.4470
c (Å)	2.9533	9.5156	5.1450
Volume	62.07	136.25	257.38
Molar volume	18.693	20.156	19.377
Density (g/cm ³)	4.2743	3.8950	4.1230
Refractive index	2.71	2.52	2.63
Hardness	6.0-7.0	5.5-6.0	5.5-6.0
Melting point	1858 °C	change to rutile at high temperature (915 °C)	change to rutile at high temperature (750 °C)

Rutile has three main crystal faces, two that are quite low in energy and are thus considered to be important for practical polycrystalline or powder materials. These are: (110) and (100) (Fig. 2.17 (a) and (b)). The most thermally stable is (110), and therefore it has been the most studied. It has rows of bridging oxygens (connected to just two Ti atoms). The corresponding Ti atoms are 6-coordinate. In contrast, there are rows of 5-coordinate Ti atoms running parallel to the rows of bridging oxygens and alternating with these. As discussed later, the exposed Ti atoms are low in electron density (Lewis acid sites). The (100) (Fig. 2.17 (b)) surface also has alternating rows of bridging oxygens and 5-coordinate Ti atoms, but these exist in a different geometric relationship with each

other. The (001) face (Fig. 2.17 (c)) is thermally less stable, restructuring above 475 °C. There are double rows of bridging oxygens alternating with single rows of exposed Ti atoms, which are of the equatorial type rather than the axial type.

Anatase has two low energy surfaces, (101) and (001) (Fig. 2.18 (a) and (b)), which are common for natural crystals. The (101) surface, which is the most prevalent face for anatase nanocrystals, is corrugated, also with alternating rows of 5-coordinate Ti atoms and bridging oxygen, which are at the edges of the corrugations. The (001) (Fig. 2.18 (b)) surface is rather flat but can undergo a (1 x 4) reconstruction. The (100) surface is less common on typical nanocrystals but is observed on rod-like anatase grown hydrothermally under basic conditions (Fig. 2.18 (c)). This surface has double rows of 5-coordinate Ti atoms alternating with double rows of bridging oxygens. It can undergo a (1 x 2) reconstruction. Recently, the brookite phase, which is rarer and more difficult to prepare, has also been studied as a photocatalyst^[69]. The order of stability of the crystal faces is (010) < (110) < (100) (Fig. 2.19).

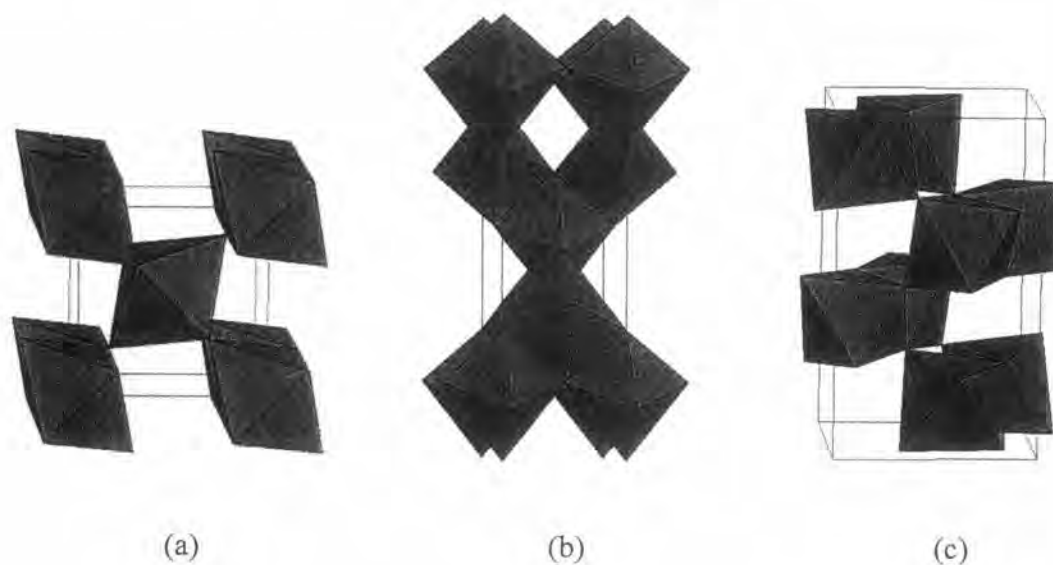


Fig. 2.16 Crystal structure of TiO₂ (a) rutile (b) anatase (c) brookite.

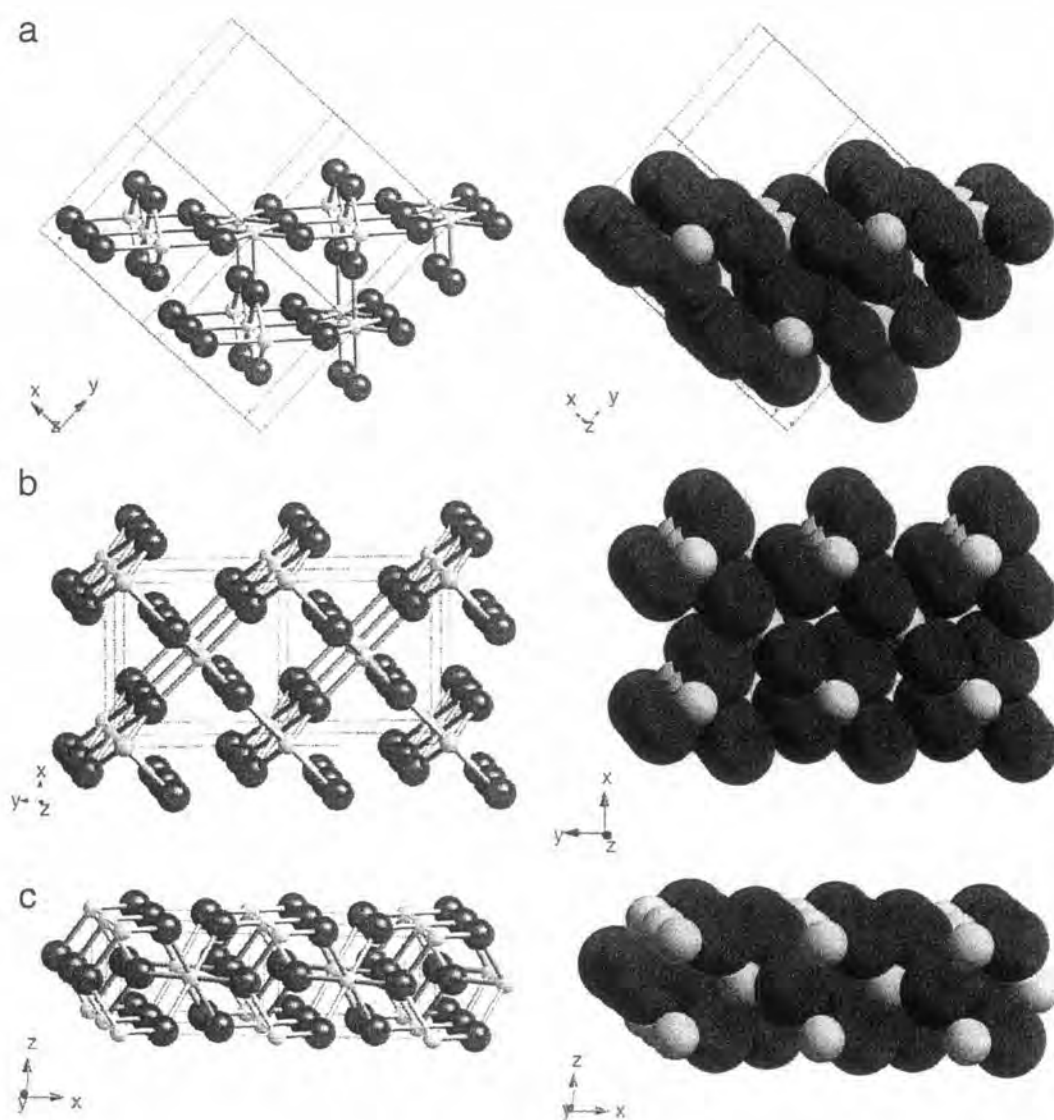


Fig. 2.17 Schematic representations of selected low-index faces of rutile: (a) (110); (b) (100); and (c) (001)^[70].

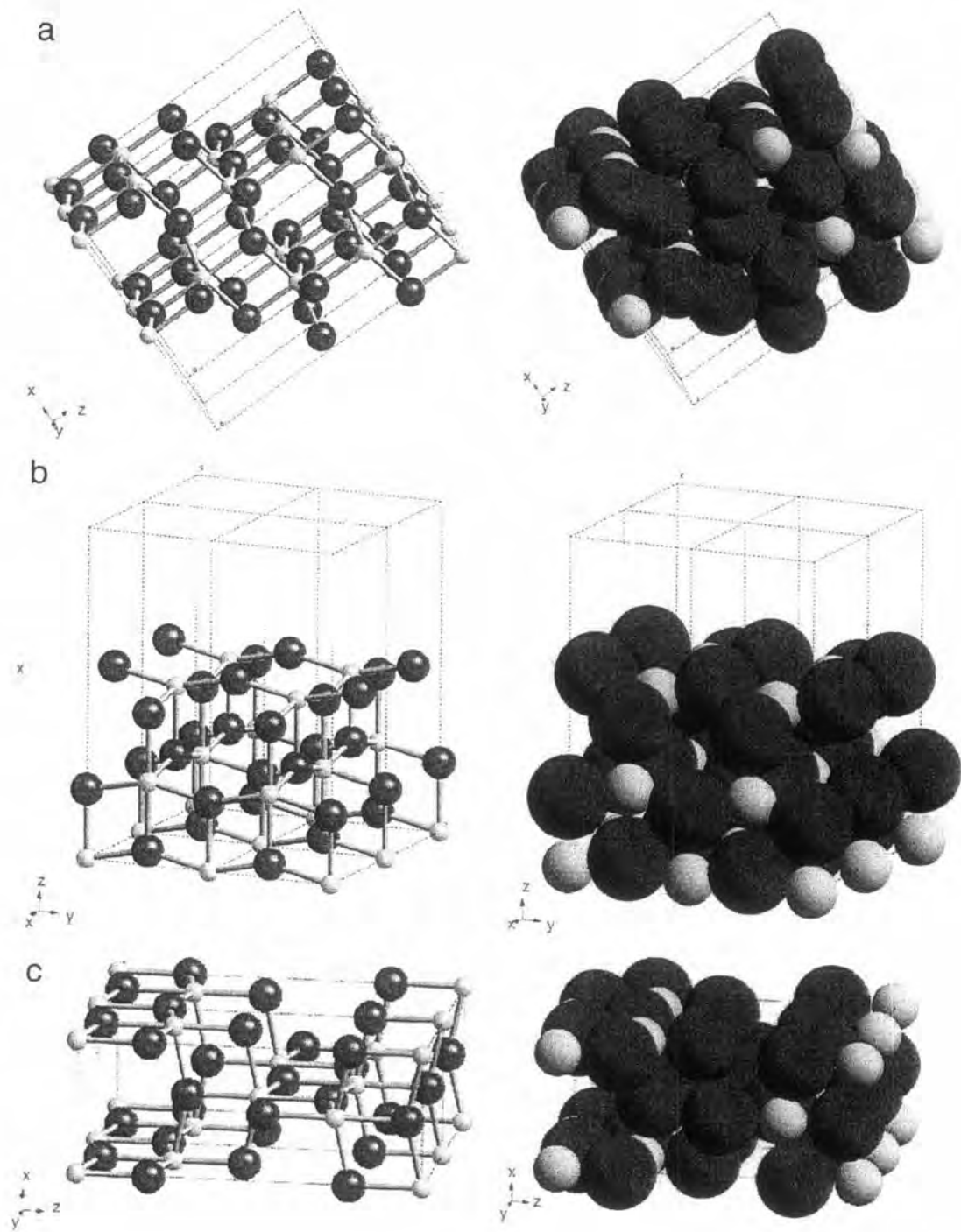


Fig. 2.18 Schematic representations of selected low-index faces of anatase: (a) (101); (b) (100); and (c) (001)^[70].

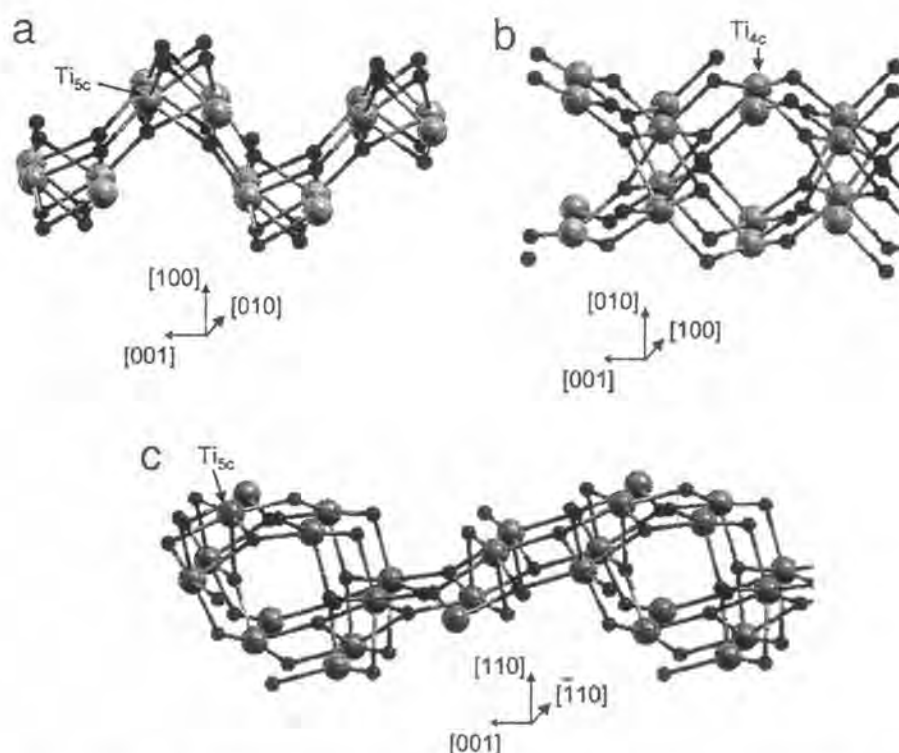


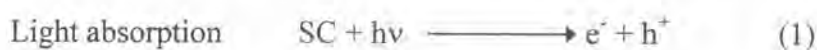
Fig. 2.19 Schematic representation of the brookite structure^[70].

B. Mechanism of TiO₂ photocatalysis^[71-74]

Photocatalysis is a change in the rate of chemical reactions or their generating under the action of light in the presence of the substances- called photocatalysts-that absorb light quanta and are involved in the chemical transformations of the reaction participants, repeatedly coming with them into intermediate interactions and regenerating their chemical composition after each cycle of such interactions. Photocatalysis can be generally divided into two classes of processes, depending on where the initial photoexcitation occurs. When the initial photoexcitation occurs in an adsorbate molecule which then interacts with the ground state catalyst substrate, the process is referred to as a catalyzed photoreaction. When the initial photoexcitation takes place in the catalyst substrate and the photoexcited catalyst then transfers an electron or energy into a ground state molecule, the process is referred to as a sensitized photoreaction.

Semiconductors can act as the substances or photocatalysts for photocatalytic reaction due to their electronic structure. The molecular orbitals of semiconductors have a band structure. Unlike metals which have a continuum electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of an electron and hole produced by photoactivation in the solid. The void energy region which extends from the top of the filled valence band to the bottom of the vacant conduction band is called the band gap energy (E_g). It is the minimum energy of light required to make the material electrically conductive, or, in other words, to get the electrons excited enough to get moving. Once excitation occurs across the band gap there is a sufficient lifetime, in the nanosecond regime, for the created electron-hole pair to undergo charge transfer to adsorbed species on the semiconductor surface from solution or gas phase contact. If the semiconductor remains intact and the charge transfer to the adsorbed species is continuous and exothermic, the process is termed heterogeneous photocatalysis.

The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductors is the generation of electron-hole pair in the semiconductor particles. Equations (1)-(4) show the possible reactions that can occur when organic and inorganic compounds containing a semiconductor (SC) absorbs a photon wide range of species can be converted via these processes.



The photoinduced electron transfer to adsorbed organic or inorganic species or to the solvent results from migration of electrons and holes to the semiconductor surface. The electron transfer process is more efficient if the species are preadsorbed on the surface. While at the surface the semiconductor can donate electrons to reduce an electron acceptor (usually oxygen in an aerated solution) (Eq. (4)); in turn, a hole can

migrate to the surface where an electron from a donor species can combine with the surface hole oxidizing the donor species (Eq. (3)). The probability and rate of the charge transfer processes for electrons and holes depends upon the respective positions of the band edges for the conduction and valence bands and the redox potential levels of the adsorbate species. In competition with charge transfer to adsorbed species is electron and hole recombination. Recombination of the separated electron and hole can occur in the volume of the semiconductor particle or on the surface with the release of heat (Eq. (2)).

Obviously electron and hole recombination is detrimental to the efficiency of a semiconductor photocatalyst. Modifications to semiconductor surfaces such as addition of metals, dopants, or combinations with other semiconductors are beneficial in decreasing the electron and hole recombination rate and thereby increasing the quantum yield of the photocatalytic process.

For oxidation to occur (Eq. (3)) the valence band must have a higher oxidation potential than the material under consideration. The redox potential of the valence and conduction bands for different semiconductors varies between +4.0 and -1.5 volts vs Normal Hydrogen Electrode (NHE) respectively. Therefore by careful selection of the semiconductor photocatalyst a wide range of species can be converted via these processes.

Firstly by careful selection of the semiconductor the redox chemistry of a particular reaction may be controlled. For example, specific transformations may be achieved by targeting functional groups on molecules. This can enable specialized products to be prepared which may not be accessible by other synthetic routes. Table 2.9 shows a list of semiconductor materials which have been used for photocatalytic reactions, together with the valence band and conduction band positions. The final column in the table indicates the wavelength of radiation required to activate the catalysts. The oxidizing and reducing powders of these materials can be compared to redox reagents traditionally used by industry with reference to Table 2.10.

Table 2.9 The band positions of some common semiconductor photocatalysts in aqueous solution

Semiconductor	Valence band (V vs NHE)	Conduction band (V vs NHE)	Band gap (eV)	Band gap wavelength (nm)
TiO ₂	+3.1	-0.1	3.2	380
SnO ₂	+4.1	+3.0	3.9	318
ZnO	+3.0	-0.2	3.2	390
ZnS	+1.4	-2.3	3.7	336
WO ₃	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	497
CdSe	+1.6	-0.1	1.7	730
GaAs	+1.0	-0.4	1.4	887
GaP	+1.3	-0.1	2.3	540

Table 2.10 Oxidation/reduction potentials of traditional industrial redox agents

Reagent	Redox potential vs NHE
Ag ²⁺	+1.98
Ce ⁴⁺	+1.72
Cr ⁶⁺	+1.33
Cl ₂	+1.36
Br ₂	+1.09
Sn ²⁺	-0.14
Ni ²⁺	-0.25
Zn ²⁺	-0.76
Al ³⁺	-1.66
Li ⁺	-3.03

A comparison of the strong oxidizing potential of the valence band of the semiconductor to the oxidizing potential of materials such as Cr⁶⁺ or Ag²⁺ suggests that semiconductors should be at least as effective oxidizing agents as these traditional reagents. In many cases the semiconductor valence band is even more strongly oxidizing

than even Ag^{2+} , therefore potentially extending the range of oxidation reactions which may be performed.

Several simple oxide and sulfide semiconductors have band-gap energies sufficient for promoting or catalyzing a wide range of chemical reactions of environmental interest. They include TiO_2 ($E_g \approx 3.2$ eV), WO_3 ($E_g \approx 2.8$ eV), SrTiO_3 ($E_g \approx 3.2$ eV), $\alpha\text{-Fe}_2\text{O}_3$ ($E_g \approx 3.1$ eV), ZnO ($E_g \approx 3.2$ eV) and ZnS ($E_g \approx 3.6$ eV). However, among these semiconductors TiO_2 has proven to be the most suitable for widespread environmental applications because it is high efficiency, nontoxic, biologically and chemically inert (stable with respect to photocorrosion and chemical corrosion) and it is inexpensive. The primary criteria for good semiconductor photocatalysts for organic compound degradation are that the redox potential of the $\text{H}_2\text{O}/\text{OH}$ ($\text{OH}^- = \text{OH} + e^-$; $E^\circ = -2.8$ V) couple lies within the band gap domain of the material and that they are stable over prolonged periods of time. The metal sulfide semiconductors are unstable based on the stability requirements in that they readily undergo photoanodic corrosion, while the iron oxide polymorphs ($\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, $\beta\text{-FeOOH}$, $\delta\text{-FeOOH}$ and $\gamma\text{-FeOOH}$) are not stable semiconductors, even though they are inexpensive and have nominally high band gap energies, because they readily undergo photocathodic corrosion. ZnO appears to be a suitable alternative to TiO_2 ; however, ZnO is unstable with respect to incongruous dissolution to yields $\text{Zn}(\text{OH})_2$ on the ZnO particle surfaces and thus leading to catalyst inactivation over time.

The mechanism of TiO_2 photocatalysis is shown in Fig. 2.20. When TiO_2 surface is illuminated by light with energy equal to or larger than the band gap energy (ΔE_{bg}), it excites the electron in the valence band to the conduction band, resulting in the formation of positive-hole (h^+) in the valence band and negative-electron (e^-) in the conduction band. The positive-hole oxidizes either pollutant directly or water molecule adsorbed on the TiO_2 surface to produce hydroxyl radical (OH^\bullet), whereas the negative-electron in the conduction band reduces oxygen adsorbed on TiO_2 surface to form superoxide anion (O_2^-). This cycle continues when light is available. The described mechanism can be represented by Equation (1)-(5) as shown below:



In the photocatalytic degradation of the pollutants, when the reduction process of oxygen (Eq. (2)) and the oxidation of pollutants (Eq. (3) and (4)) do not proceed simultaneously, there is an electron accumulation in the conduction band, thereby causing a recombination of negative electron and positive holes. Therefore, efficient consumption of electron is essential to promote photocatalytic oxidation.

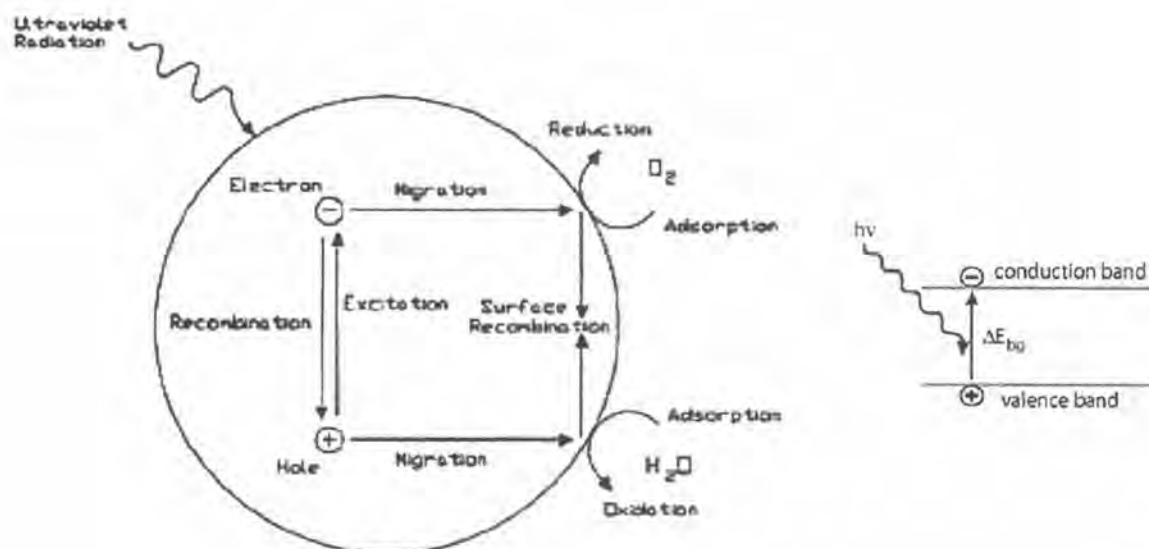


Fig. 2.20 Schematic representation of the mechanism of TiO_2 photocatalysis.
(photochemical activation and electron-hole formation)

In the photocatalytic degradation of the pollutants, when the reduction process of oxygen (Eq. (2)) and the oxidation of pollutants (Eq. (3) and (4)) do not proceed

simultaneously, there is an electron accumulation in the conduction band, thereby causing a recombination of negative electron and positive holes. Therefore, efficient consumption of electron is essential to promote photocatalytic oxidation.

The TiO_2 of the anatase type generally shows a higher photocatalytic than the other types of TiO_2 . One of the reasons the anatase type titanium dioxide is more photoactive than the rutile type may lay in the differences in their so called energy band structures. For anatase-type titanium dioxide this energy is 3.2 electron volts (eV), which corresponds to UV light (380 nm), while the band gap energy for the rutile type is 3.0 eV, corresponding to violet light (413 nm). In more technical terminology, the band gap energy for a semiconductor indicates the minimum energy of light necessary to produce conduction band (CB) electrons, which, for example, can give rise to electrical conductivity (photoconductivity) and valence band (VB) "hole," which are actually the absence of electron. These holes can react with water to produce the highly reactive hydroxyl radical (OH^\bullet). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic materials. The level of the CB for anatase turns out to be 0.2 eV higher than that for rutile.

The VB energies for anatase and rutile are both similar, which is very low in the energy diagram, meaning that, for both materials, the VB holes (and the hydroxyl radicals) have great oxidizing power. The CB energy for rutile is close to the potential required to electrically reduce water to hydrogen gas, but that for anatase is higher in the energy diagram, meaning that it has higher reducing power. This means that it can drive the very important reaction involving the electrolytic reduction of molecular oxygen (O_2) to superoxide (O_2^-). Several research groups have found that superoxide is almost as important as the holes and hydroxyl radicals in breaking down organic compounds.

C. Applications of TiO_2 photocatalysis

TiO_2 photocatalysis has great potential to use in a variety of applications (Table 2.11). Some practical applications are as follows:

1. Self-cleaning

The TiO_2 surface can decompose organic contamination with the aid of ultraviolet light. This observation suggests the application of TiO_2 photocatalysis to a novel “self-cleaning” technique, i.e., a surface coated with TiO_2 can maintain itself clean under ultraviolet illumination (Fig. 2.21). This technique is obviously of great value, since it can utilize freely available solar light or waste ultraviolet emission from fluorescent lamps, save maintenance costs and reduce the use of detergents.

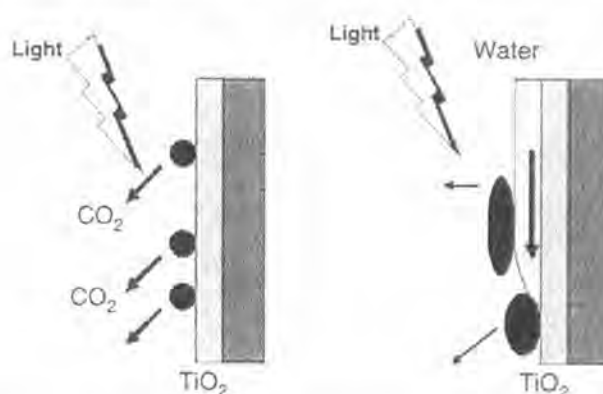


Fig. 2.21 Schematic diagram of the decontamination process occurring on the superhydrophilic self-cleaning surface.

The efficacy of self-cleaning surfaces was found to be dependent on the relative rates of decontamination vs. contamination. The TiO_2 photocatalyst can maintain the surface clean only when the photocatalytic decontamination rate is greater than that of contamination. However, the self-cleaning effect of TiO_2 surfaces could be enhanced when water flow, such as natural rainfall, was applied to the surface. Wang et al. attributed this enhancing phenomenon of water flow to the superhydrophilic property of TiO_2 surface, i.e., water penetrated the molecular-level space between the stain and the superhydrophilic TiO_2 surface. In other words, this phenomenon has effectively removed the limitation of the self-cleaning function of TiO_2 photocatalysis set by the number of incident photons. Even though the number of photons may be insufficient to decompose the adsorbed stain, the surface is maintained clean when water is supplied there. Thus, the best use of self-cleaning TiO_2 surfaces should be exterior construction materials, such as

tiles, glass, aluminium sliding, plastic films, tent materials and cement, since these materials could be exposed to abundant sunlight and natural rainfall.

2. Water purification

One of the advantages of TiO_2 photocatalysis for water decontamination is that only the TiO_2 photocatalyst (immobilized or suspended) and UV light, either from solar light or artificial light source, are needed and thus its cost can be lower than other kinds of advanced oxidation techniques (UV/ O_3 , UV/ H_2O_2 , photo-Fenton). Moreover, no toxic intermediate products are generated in the photocatalytic decontamination process; this makes it very attractive for cleaning the water environment, even for cleaning drinking water. However, it is generally accepted that TiO_2 photocatalysis is feasible only for the treatment of wastewater that contains contaminations at low to medium pollutant concentrations, because of its relatively low efficiency and the limited flux of ultraviolet photons.

Other important water-purification applications of TiO_2 photocatalysis include water disinfection, remediation of metal contamination and oxidation of arsenite. For developing countries, solar photocatalytic disinfection appears to be a promising process to produce drinking water, which could help in improving public health.

3. Air purification

One of the most important applications of TiO_2 photocatalysis is to decontaminate, deodorize and disinfect indoor air. Low-concentration volatile organic compounds (VOCs), such as formaldehyde and toluene, emitted from interior furnishings and construction materials, may lead to the "sick building syndrome" and other diseases. Besides, the indoor air of public facilities, which is normally contaminated with bacteria, fungi, etc., threatens the health of users. Conventional air-purification systems often adapt filter-type components for the cleaning of polluted air. Pollutants are accumulated in the active carbon filters, and the filter becomes saturated with adsorbed substances and loses its function after a certain period of use. Treatment of the used air filters may cause the risk of secondary pollution. Photocatalytic air-cleaning filters, however, can

decompose the organic substances instead of accumulating them and, as a result, exhibit performance than conventional ones. Moreover, the photocatalytic filter can kill the bacteria floating in indoor air, which is also important for indoor air purification.

Fig. 2.22 shows images of two types of photocatalytic filters used in air-purification devices. The filters feature either a honeycomb-type construction or a three-dimensional porous structure for minimum pressure drop. TiO_2 nanoparticles are coated on the body of the filter with active carbon, zeolite, etc., as co-adsorbents. The co-adsorbents facilitate the adsorption of VOCs on the filter, and ensure that no intermediate gaseous compounds diffuse into the ambient atmosphere. The adsorbed substances diffuse on the surface of the adsorbent until they reach the TiO_2 and then undergo photodecomposition. The oxidizing species on the photocatalyst can also diffuse to the surface of the adsorbent and participate in oxidation reactions there. UV light, illuminated on the filter surface from black-light lamps, is generally at the level of several mW/cm^2 ; this ensures the rapid mineralization of VOCs that typically exist in concentrations of about 1ppm or even lower. After long-term use, the filter may be poisoned by HNO_3 or H_2SO_4 formed during removal of ammonia or hydrogen sulfide. In such a case, the poisoned filter can be regenerated by simply washing with water.

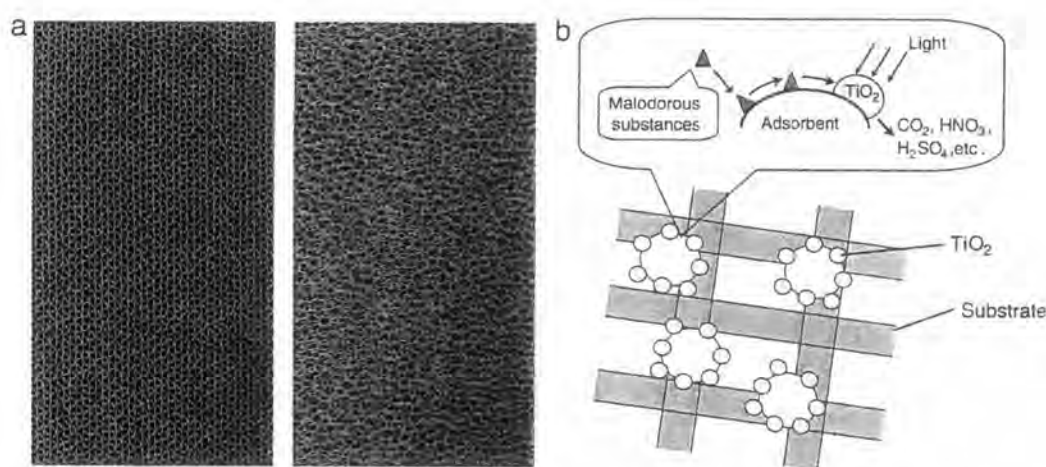


Fig. 2.22 (a) Photographic images of a honeycomb-type air-cleaning filter (left) and a three-dimensional porous ceramic air-cleaning filter (right); (b) Schematic diagram of the microscopic structure of the air-cleaning filter; the substrate materials (ceramics, paper, fabrics) are coated with a composite of TiO_2 and adsorbent.

4. Self-sterilizing

TiO₂ photocatalysts can kill bacteria on their surfaces, and therefore self-sterilizing surfaces can be prepared. Such materials are particularly useful for hospitals and elder care facilities, where the control of surface and airborne bacteria and viruses is important. One advantage of photocatalytic sterilizing surfaces is that they operate in a passive fashion, that is, without the need for electrical power or chemical reagents, only light and oxygen being required. Unlike chemical antibacterial agents, TiO₂ surfaces are non-poisonous and will not result in environmental pollution. It is thus expected in the near future that self-sterilizing TiO₂ materials may have many medical applications. At least, hospital room walls, medical instruments, and hospital uniforms can all be coated with self-sterilizing TiO₂ materials.

5. Anti-fogging

The fogging of the surfaces of mirrors and glass occurs when moist air cools down on these surfaces, forming many water droplets. These droplets, ranging from micrometer to millimeter size, tend either to scatter light or simply to reflect or refract it randomly. In both cases, visual clarity is impaired drastically. In a serendipitous discovery, Watanabe and co-workers found that a TiO₂-SiO₂ surface could become extremely hydrophilic under UV illumination. The result of this property is that water spreads evenly across the surface. If the amount of water is relatively small, the water layer becomes very thin and evaporates quickly. If the amount of water is larger, it forms a sheet-like layer that also has high visual clarity (Fig. 2.23). The first commercial application of this phenomenon has been for automotive side-view mirrors.

The uses of anti-fogging technology, however, are not limited to mirrors and glass. One example in our daily life is air conditioners. When an air conditioner is operating to cool during the summer, air that is cooled on the heat exchanger of the air conditioner often has moisture condensing out of it, except in an extremely dry climate. For an ordinary plate heat exchanger, the condensed water droplets fog the fins and large water droplets often form, often bridging between the adjacent fins; this can reduce the heat exchange efficiency and increase the resistance to air flow. Coating the heat

exchanger surface with superhydrophilic TiO_2 , however can hinder the fogging and the formation of water bridging, and remove the condensed water more effectively.

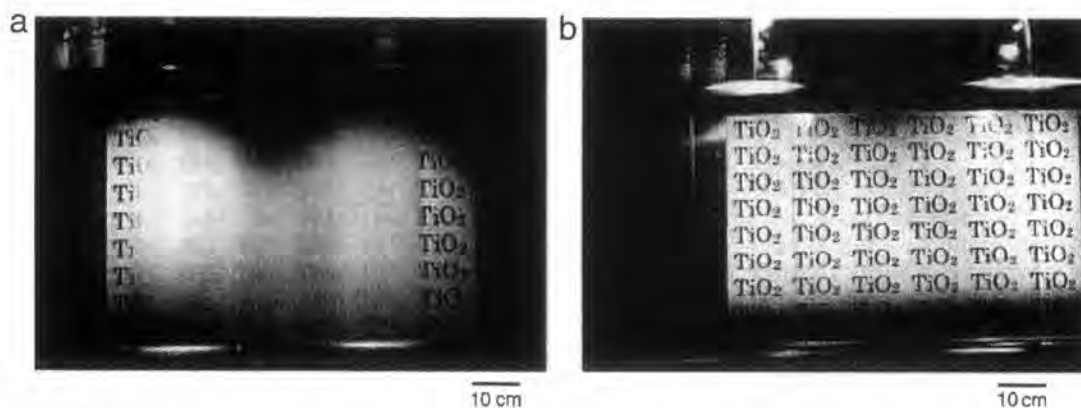


Fig. 2.23 Photographs of fogged surfaces of usual glass (a) and TiO_2 -coated glass after sufficient UV illumination (b), typically > 150 min at an intensity of 1 mW/cm^2 .

6. Heat transfer and heat dissipation

Superhydrophilic surfaces may improve the heat transfer accompanied by liquid-vapor-phase transition. Takata et al. studied the heat transfer properties of superhydrophilic TiO_2 surfaces. They found that a TiO_2 -coated Cu cylinder exhibited excellent heat transfer characteristics in the nucleated boiling regime, and its critical heat flux (CHF), a condition where liquid cannot rewet the heater wall because of the rate of vapor production impeding the liquid flow back to the hot surface, was about two times higher than that of the uncoated surface. They also compared the falling-film evaporation on a superhydrophilic surface with that on an ordinary surface. In this work, water was sprayed on the heated surface through nozzles to form a water film. They found that on the superhydrophilic surface, a stable water film was formed for much smaller water flow rates than those on an ordinary surface. Since the heat transfer rate increases for thinner water films, the superhydrophilic surface is expected to improve the performance of falling-film evaporators, which are widely used in seawater desalination units and milk and juice concentrators. They observed that the superhydrophilic surface performed 40 times better than the ordinary surface in low water flow and low heat flux. For high water flow, a thick water film formed on both the superhydrophilic and the ordinary surface,

and thus no difference in heat transfer rate was observed. These workers suggested that the superhydrophilic surface could be an ideal heat transfer surface and would be applicable to various heat transfer phenomena that are affected by surface wettability.

Hashimoto et al. reported recently the cooling of the exterior walls of buildings with a falling-water film, with the intent to help resolve the urban heat island problem for major cities and to reduce the electricity consumption by air conditioners in summer. In their experiments, water was continuously sprinkled onto the surfaces of buildings that were covered with TiO_2 films. Due to the superhydrophilic property of the material, water was able to spread on the surfaces in the form of a thin water film (~ 0.1 mm). The evaporation of the water film can effectively cool the building surface and also the surrounding air. They observed on a clear day in the middle of summer that the temperature drops were 15°C on window glass and $40\text{--}50^\circ\text{C}$ on black-roof-tile surfaces. The cooling of the building surfaces is expected to result in the reduction of electricity consumption by air conditioners. As estimated by Hashimoto et al., this reduction could be ten to several tens of percentage for a real house. Therefore, TiO_2 -coated building materials could contribute much to energy-saving technologies in the future (Fig. 2.24). The water film is so thin that only a small amount of water is required to cover the building surfaces. Moreover, natural rainwater can be collected and stored in specially designed reservoirs for this purpose so that the cost of the water can be reduced. The water film also helps in maintaining the building surface clean by the self-cleaning effect.

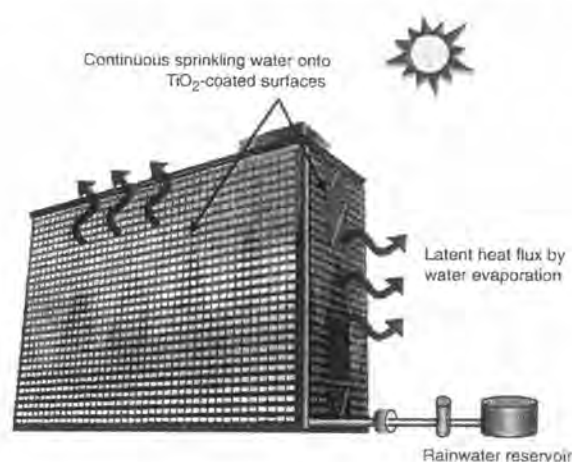


Fig. 2.24 Energy-saving system using solar light and stored rainwater.

7. Anticorrosion applications

In general, metals are protected from corrosion in several ways, for example, by a corresponding passive metal compound layer, by paint layer, or by a sacrificial metal coating (with a less positive corrosion potential). Of these the passive layer and the paint layer are effective only when the coating covers the metal surface perfectly. As for the sacrificial metal coating, its lifetime is limited, because the metal coating dissolves gradually. Recently, the application of photocatalytic technology in corrosion prevention for metals has been examined.

In cooperation with the Koyo Electrical Construction Co., Ohko et al. studied the anticorrosion effects of a TiO₂ coating for Type 304 stainless steel. Under UV irradiation, TiO₂ injected electrons into the steel and as a result protected it from corrosion, while the photogenerated holes decomposed organic contaminants to provide a self-cleaning function. Interestingly, the coating remained effective even if performed with pinholes.

8. Environmentally friendly surface treatment

In conventional technology for manufacturing printed circuit boards (PCBs), insulating resin materials are etched with strong oxidants such as permanganate and hexavalent chromium to prepare rough surfaces followed by electroless plating of a copper layer on the whole surface and removal of the unwanted copper after applying a temporary mask. The surface treatment procedure is of vital importance for the strong adherence of the copper layer to the resin substance. However, the use of those oxidants can cause serious environmental problems. Moreover, the roughness of the etched surface is often of the order of micrometers, which can lead to technical problems in the fabrication of fine copper wires. Honma and co-workers recently reported a novel environmentally friendly surface treatment technique for PCB manufacture by treatment of resin surfaces with TiO₂ photocatalyst, replacing conventional etchants. They found that an aqueous TiO₂ suspension was able to oxidize an epoxy resin surface within a depth of 30-50 nm under UV illumination but did not affect surface roughness appreciably. Palladium and tin catalysts for the electroless position of copper penetrated into the surface-modified layer and electroless copper plating was initiated at the bottom

of this layer. As a result, the copper layer showed excellent adhesion (1.15 kN/m) to the epoxy surface, even better than that obtained by conventional technology. By using this new surface treatment technique, Honma et al. succeeded in fabricating fine patterns of copper with lines and spaces of 10 μm / 10 μm , as shown in Fig. 2.25.

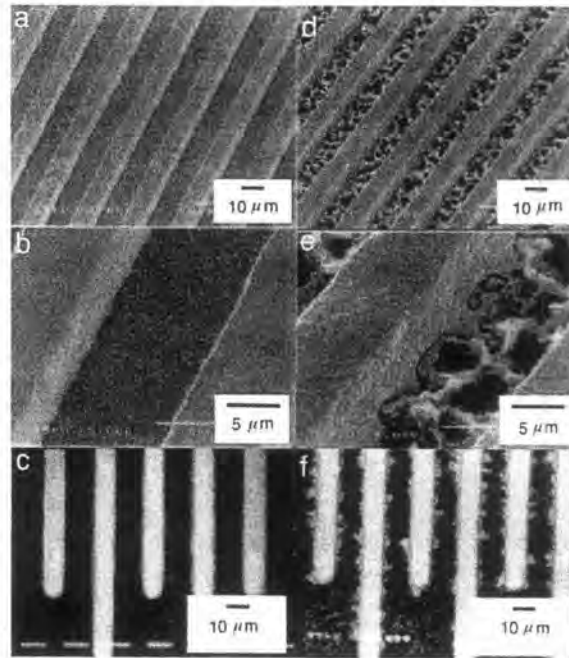


Fig. 2.25 SEM mapping of 10 mm=10 mmL/S copper wiring. (a)-(c) PCB substrates were treated by TiO_2 photocatalyst. (d)-(f) PCB substrates were etched with permanganate etching process. (c) and (f) are reflection mode images. As shown, the photocatalytic treatment did not change the surface morphology of PCB much, and could be used to prepare finer copper wires than those obtained by the conventional etching method.

9. Photocatalytic lithography

The active oxygen species such as the hydroxyl radical or singlet O_2 generated during the photocatalytic process are so active that they can oxidize not only organic materials but also inorganic materials such as copper, silicon, carbon, and SiC etc. The oxidation can occur either on the TiO_2 surface or at a distance away from the surface. Therefore, it is possible to develop a novel photocatalytic lithographic method based on

the oxidation reactions to fabricate surface patterns with composition/wettability contrast. This novel method would have the advantages of simplicity and low cost: it does not require expensive photo-resist materials and special equipment.

10. Photochromism

Photochromic materials, which change their colors reversibly in response to light, can be applied to smart windows, displays and memories. Conventional photochromic materials respond in a monochromatic way, so that multicolor photochromism has required several different materials or filters combined appropriately. If multicolor photochromism could be achieved with a simple material, photochromic devices would find a greater number of applications, including a rewritable color copy paper or electronic paper and a high-density multi-wavelength optical memory. Ohko et al. recently reported the interesting multicolor photochromism of TiO_2 films loaded with silver nanoparticles. The film color, initially brownish-grey, changed under monochromatic visible to almost the same color as that of the light (Fig. 2.26); the apparently uniform Ag-TiO_2 film can take on almost any color. The color reverted to brownish-grey under ultraviolet light, and these processes were found to be repeatable.



Fig. 2.26 A thick multicolored Ag-TiO_2 film. Each spot (6 mm diameter) was irradiated successively with a blue, green, red, or white light.

Ohko et al. proposed the following model for the multicoloring process: on irradiation with monochromatic visible light, the corresponding Ag nanoparticles adsorb the light, and the electrons thus excited are accepted by O_2 , resulting in oxidation of the

Ag nanoparticles to Ag^+ and an absorption decrease appears at the corresponding wavelength, i.e., the color of the excitation wavelength. The most important role of the TiO_2 film is the repeatable generation of Ag nanoparticles with diverse sizes and shapes due to the “molding effect” of the nanoporous TiO_2 film; this resulted in different plasmon resonance absorption wavelength of the Ag particles in the whole visible light spectrum.

11. Microchemical systems

Microchemical systems using microchannels as reaction fields provide many technical advantages over conventional technologies for chemical synthesis as well as analysis. Coating the inner walls of microchannels with TiO_2 provides photocatalytic reactivity to microchemical systems. Possible applications include the photocatalytic degradation of organic pollutants, photocatalytic synthesis of organic compounds, site-selective introduction of functional metal nanoparticles, photo-controllable wettability of channels, and self-cleaning microchannels, among others.

Table 2.11 Some applications of TiO₂ photocatalysis

Property	Category	Application
Self-cleaning	Materials for residential and office buildings	Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, aluminum siding, building stone and curtains, paper window blinds
	Indoor and outdoor lamps and related systems	Translucent paper for indoor lamp covers, coatings on fluorescent lamps and highway tunnel lamp cover glass
	Materials for roads	Tunnel wall, soundproofed wall, traffic signs and reflectors
	Others	Tent material, spray coatings for car, cloth for hospital garments and uniforms
Air cleaning	Indoor air cleaners	Room air cleaner, photocatalyst-equipped air conditioners and interior air cleaner for factories
	Outdoor air purifiers	Concrete for highways, roadways and footpaths, tunnel walls, soundproof walls and building walls
Water purification	Drinking water	River water, ground water, lakes and water-storage tanks
	Others	Fish feeding tanks, drainage water and industrial wastewater
Antitumor activity	Cancer therapy	Endoscopic-like instruments
Self-sterilizing	Hospital	Tiles to cover the floor and walls of operating rooms, silicone rubber for medical catheters and hospital garments and uniforms