Porous crystals: a perspective

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Abstract – Crystals porous on the scale of molecules are found among aluminosilicates, crystalline silicas, aluminophosphates, expanded clay minerals, clathrates and metallocyanates. Properties shared by all types are host crystal stabilisation by guest molecules; and shape-selective uptake of guest. Zeolites, expanded clay minerals, and porous aluminophosphates part substituted by Si or by metals, have catalytic properties, while zeolites and clay minerals share cation exchange properties. Some of these properties are illustrated and discussed.

INTRODUCTION

My aim in this paper is to give some perspective to the science of crystals porous on the scale of molecules. Categories of such crystals include:

(i) Porous aluminosilicates ⟨ Zeolites / Salt-bearing felspathoids
(and Ga and Ge analogues)

(ii) Crystalline porosils ⟨ Open channel types (zeosils) / Clathrate types (clathrasils)

(iii) Porous aluminium phosphates ⟨ $AlPO_4$'s (AlPO's) / $(Si,Al,P)O_4$'s (SAPO's) / $(M,Al,P)O_4$'s (MAPO's) (M = metal)

(iv) Permanently expanded clay minerals ⟨ Smectite-based / Vermiculite-based

(v) Clathrates

(vi) Werner compounds

These classes of porous crystals provide many elegant examples of 1-, 2- and 3-dimensional channel systems freely accessible to molecules of appropriate shape and size; and of structures where well-defined cavities are present, linked through windows wide enough to allow molecules to migrate between cavities; or where the shared windows are not wide enough for molecule migration, as in clathrasils and clathrates.

THE HOST–GUEST RELATIONSHIP

These porous crystals are characterised by a continuous "host" structure, within which "guest" molecules may be present. In their synthesis the guest can and normally does play a vital role. In thermodynamic terms it lowers the chemical potential of the lattice-forming units of the host by forming with it a type of solid solution, and so stabilises the porous host structure with respect to the empty host and also to non-porous alternate structures which could and would crystallise in absence of the guest [1]. In aluminous zeolites the guest molecule involved in synthesis is water. Indeed zeolitic water is a space-filling catalyst in the classical definition of catalyst: the reaction desired will not occur in its absence; and after the reaction the water may be removed unchanged leaving behind the stable porous host structure. If the zeolites are made more and more silica rich they become less hydrophilic and more organophilic. As a result Si-rich zeolites in particular are stabilised in synthesis by various organic species added to the reaction mixtures, which increasingly replace water as the guest.

Apart from the fundamental thermodynamic role played by the guest molecules another very specific role is often apparent: that of a template species which directs nucleation and

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growth of the host crystals to favour particular framework topologies [2,3]. This is especially in evidence among siliceous zeolites, porosils, AlPO's and clathrates. The templating function may be illustrated taking the clathrasils as the example [4]. Their very strong stable frameworks can be constructed by stacking polyhedra, so as to fill all space. Thus in silica-sodalite there are 14-hedra with 6 x 4-ring and 8 x 6-ring faces, designated therefore as a $4^6 6^8$ polyhedron. With this notation one has the description of several clathrasils given in Table 1.

TABLE 1. Structural features of some clathrasils

Clathrasil	Polyhedra	Polyhedra per Unit Cell	Shape	Free dimensions $\overset{\circ}{A}$
Melanophlogite (46 SiO_2 per unit cell)	5^{12} $5^{12} 6^2$	2 6	spheroidal rotation ellipsoid	~5.7 ~5.8 x 7.7
Silica-sodalite (12 SiO_2 per unit cell)	$4^6 6^8$	2	spheroidal	~6.6
Dodecasil 3C (136 SiO_2 per unit cell)	5^{12} $5^{12} 6^4$	16 8	spheroidal spheroidal	~5.7 ~7.5
Dodecasil 1H (34 SiO_2 per unit cell)	5^{12} $4^3 5^6 6^3$ $5^{12} 6^8$	3 2 1	spheroidal spheroidal rotation ellipsoid	~5.7 ~5.7 ~7.7 x11.2

Fig. 1 [4] shows four of the polyhedra of Table 1 each containing a guest molecule of dimensions appropriate for it to act as a template, as indeed it does [4]. Because only 4- 5- or 6-ring faces are present, which are too small for guest molecules to pass through, the cages must have formed around the guest, either as units in solution needed in the formation of nuclei, or at the crystal solution interface during growth of the crystals (or both). The silica units involved in "packaging" the guest by forming a polyhedron around it could thus be small, for example monomeric $Si(OH)_4$. Evidence of template roles in zeolite syntheses and in syntheses of AlPO's has been given elsewhere [2,3,5]. In clathration this role is fundamental to success in making the host lattice, and moreover (unlike zeolites, porosils, AlPO's and expanded clays) removal of the guest from the host lattice almost invariably leads to collapse of the host into a more compact crystal structure. The bonds tying the host molecules into a continuous but porous structure are usually too weak to sustain this structure if it is not supported by the intracrystalline guest species.

COMPARISON OF SOME TYPES OF POROUS CRYSTAL

For several properties of rather special importance for technological uses, a qualitative comparison is made in Table 2 in the case of several of the categories of porous crystal referred to in §1. For the properties indicated the zeolites can show, according to the Si/Al ratios, a wide range in behaviour but at one end or the other of the spectrum of Si/Al values there are zeolites for which the property concerned is at its best. Thus the aluminous zeolites are excellent desiccants whereas the most siliceous zeolites, like the porosils, tend to be organophilic non-polar sorbents. Again, the aluminous zeolites such as Na-X, are catalysts under alkaline conditions, as in the oxidation of $H_2 S$ in air to give elemental sulphur. Where, as in a wide spectrum of uses, acidic centres are required, one moves to more siliceous zeolites which have stable hydrogen or hydronium forms. As the Si/Al ratios continue to increase the catalytic activity often tends to pass through a maximum because of two opposing effects: increased effectiveness of each acid centre on the one hand; and decreasing number of acid centres on the other.

The expanded clay minerals also show good catalytic activities, although their lesser thermal and hydrothermal stabilities suggest that their successes would be among reactions which occur at lower temperatures than are involved in some of the operations of the petrocarbon industry. They are currently attracting much interest both as sorbents and potentially useful catalysts. Their internal areas mostly fall in the range 150 to 400 $m^2 g^{-1}$, as compared with around 400 to 850 $m^2 g^{-1}$ for zeolites and for porosils like silicalites I and II. Their areas are adequate for technical applications and their moderate polarity makes them easier to outgas than the aluminous zeolites.

The AlPO's have in a number of structures internal areas which fall in the zeolite range (egs AlPO -5, -11, -31, -17, -18, and -14), with molecular sieving actions that vary according
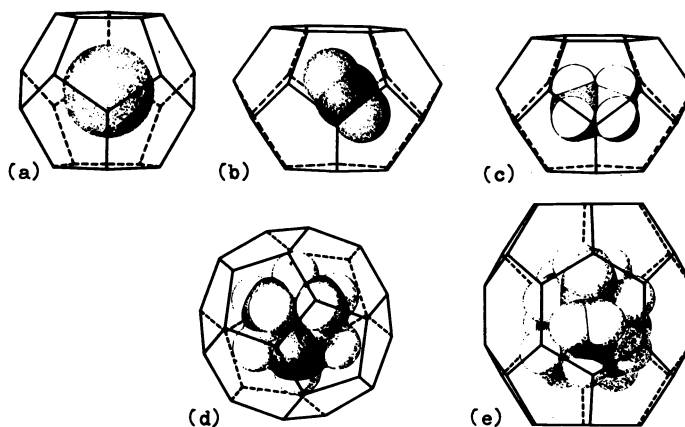
Fig. 1. Guest molecules in cages of several of the types found in clathrasils. (a) Xe in 5^{12} polyhedron of melanophlogite; (b) CO_2 in $5^{12}6^2$ polyhedron of melanophlogite; (c) CH_3NH_2 in the same polyhedron; (d) piperidine in $5^{12}6^4$ of dodecasil 3C; and (e) adamantylamine in $5^{12}6^8$ of dodecasil 1H. From ref. 4, with permission.

TABLE 2. Comparison of some properties of porous crystals

Property	Pillared Clay Minerals	Zeolites		Porosils	
		Low Si/Al	High Si/Al		
Stabilities:					
to acids	Low	Low	Mod. to v.good	v.good	Mod.
to alkalis	Mod. to low	Good	Mod. to low	mod. to low	Low
thermal	Mod.	Good	v. good	v.good	v.good
hydrothermal	Low	Low to mod.	Mod. to good	Good	v.good
Polarity	Mod.	High to mod.	Mod. to low	Low	Mod.
Catalytic activity	Yes	Yes	Yes	No	Limited *
Catalyst carriers	Yes	Yes	Yes	Yes	Yes

* SAPO's and MAPO's, however, have acid centres and function as catalysts (see later)

to the framework topologies [6] as with the other categories of porous crystal referred to in §1 (see §4). Their polarity is below that found in the aluminous zeolites so that water affinity and outgassing problems should be less severe than in some aluminous zeolites. This in turn indicates that they will not be as good desiccants as zeolite A, for example, but could find applications in separating components of organic mixtures.

In the more open zeolites, porosils and AlPO's and in pillared clay minerals, it should be possible to deposit metal atoms as single atoms or as small atomic clusters. This is well known among zeolites into which Ru, Rh, Pt, Pd, Co, Ni or Fe may be deposited by cation exchange followed by reduction, or by imbibition as carbonyls or other volatile compounds followed by thermal decomposition of the imbibed species. The result can be a bi-functional catalyst in which H-zeolite and metal each exerts its characteristic catalytic properties. The metal may be atomically dispersed, or may form clusters within or outside the zeolite. There is evidence, for example, that Ru atoms in clusters external to H-Y may be transferred back into the crystals of Y by the action of CO, or from within the crystals to the exterior by exposure to H_2O vapour [7].

Bi-functional catalysts of kinds similar to those made from zeolites plus metals should also be formed using pillared clay minerals, since these minerals can also have Bronsted acid sites. On the other hand from porosils and AlPO's one would expect that only the catalytic function of the metal atoms or clusters would be exercised because, at least in ideal crystals, there should be no intracrystalline Bronsted acid sites. In such catalysts made with expanded clays, there could be shape-selectivity in the catalysed reactions, as has already

been found in zeolite catalysts.   Thus in metal-zeolite catalysts of Fischer-Tropsch type
the mean carbon number of the hydrocarbons produced from synthesis gas ($CO+H_2$) can be in-
fluenced, inter alia, by the channel and cavity dimensions, as are the distributions and
yields among the components of the hydrocarbon mixtures formed [8].

The limited catalytic activity of AlPO's was indicated in Table 2.   These crystals may be
considered to be composed of AlO_2^- and PO_2^+ units so that in ideal crystals of composition
$AlPO_4$ there should be no nett framework charge and no intracrystalline acid sites.   However,
in SAPO's it is believed that there is some substitution of PO_2^+ by SiO_2 [9], leading to nett
negative framework charge and so to acid centres (there may also be substitutions $2SiO_2 \rightleftharpoons$
AlO_2^- $+PO_2^+$ which would not create acid centres).   Also, when salts of certain metals such
as Co^{II}, Zn^{II}, Mn^{II} and Mg^{II} are introduced into the reaction mixtures it is considered that
there is replacement of some AlO_2^- by $M^{II}O_2^{2-}$ during crystallisation, again creating framework
charge and acid centres [10].   Co-AlPO-5 and Co-AlPO-11 both converted methanol to hydro-
carbon products.   The first of these structures has 12-ring openings of free diameters ~8 Å
and the second has openings of ~6.1 Å.   The pattern of hydrocarbons formed was different for
the two catalysts.   A SAPO-5 gave the same pattern as Co-AlPO-5.   On the other hand, AlPO-5
and AlPO-11 under the same reaction conditions gave only dimethyl ether and water, verifying
the absence of acid centres.

EXAMPLES OF SHAPE AND SIZE SELECTIVITY

Shape and size selectivity in catalysts emphasises steric restrictions imposed by the zeolite
structure upon the ability of potential reactants to reach intracrystalline catalytic centres
and upon their conformations and spatial arrangements at these centres.   We briefly illus-
trate molecule sieving selectivities as exemplified by a number or numbers of several of
those categories   which are less well known than zeolites.

(i)   Among numerous other Werner-type compounds which form inclusion complexes, the cyano-
metallates form an interesting group, some with molecular sieve potential.   Thus water-free
$Zn_3[Co(CN)_6]_2$, obtained by outgassing at 310°C, readily sorbs n-hexane and 3-methylpentane,
but not 2,2-dimethyl butane, as shown in Fig. 2 for the latter two hydrocarbons [1].   It is
particularly interesting that the host lattice is based not upon the tetrahedron but upon the
octahedron.   The channels have pore openings estimated at ~ 5.6 x 8.6 Å. $Zn[Fe(CN)_5 NO]$ has
smaller openings and readily separates CO_2 from CH_4 [11,12].

(ii)   Clathration may be exemplified by Dianin's compound, (4-p-hydroxy-phenol-2,2,4-tri-
methyl chroman) and its thia analogue.   Whether in presence or absence of guest these com-
pounds crystallise to form hour-glass shaped cavities formally represented in Fig. 3 [13].
The length of the cavity is somewhat less than the C-repeat distance, ~ 11 Å, of the unit
cell.   As a consequence of the cavity dimensions one finds [14]:

molecules which fit	molecules which do not fit
n-C_6 , n-C_7	n-C_8
2-Me-C_6 , 2-Me-C_5	3-Me-C_6 ; 3-Me-C_5
2,5-diMe-C_6	2,2-diMe-C_4 ; 2,3-diMe-C_5
	2,2,3-triMe-C_4 ; e-Et-C_5
(Me = methyl)	2,4-diMe-C_6 ; 2,2,4-triMe-C_5

Thus one has the remarkable capability not only of selecting certain isomers from others,
but of making a cut of paraffins up to n-C_7 from n-C_8 on.   The selectivity for clathration
demonstrated among branched chain isomers is due to the "waist" in the cavity.   If a methyl
or ethyl group is near the middle of the backbone chain of the guest, it is obstructed by
the waist and clathration cannot occur.

(iii)   For some AlPO's free of organic template and a group of sorbate molecules, molecular
sieve cut-off's have been recorded as follows [6]:

AlPO number:

	5 and 31	11	17,18	14
H_2O				
O_2	sorbed	sorbed	sorbed	sorbed
Xe				
n-butane				← cut off
n-hexane				
iso-butane			← cut off	
cyclo-hexane		← cut off		
neo-pentane				

These orienting measurements confirm the close parallel between AlPO's and zeolites.
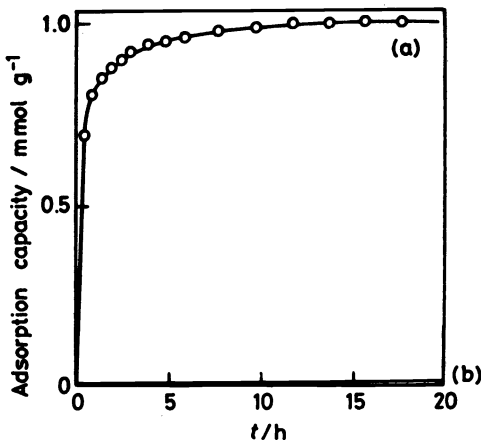
Fig. 2. Sorption of 3-Me-pentane (a) and exclusion of 2,2-di-Me-butane (b) (Me = methyl) from $Zn_3[Co(CN)_6]_2$, at $50°C$ and 40 kPa pressure [11].
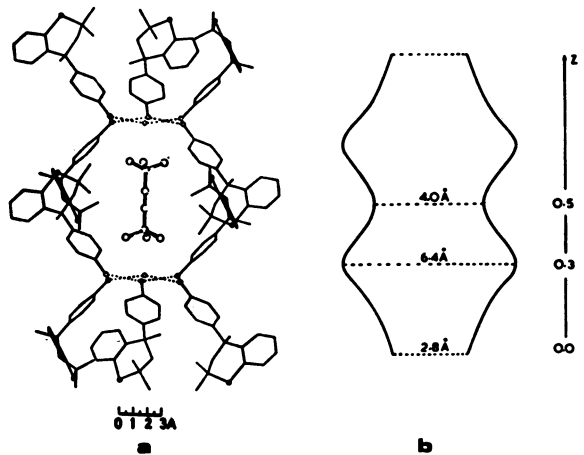
Fig. 3. (a) Structure of Dianin's compound (thia analogue) projected along the a axis, showing 2,5,5-trimethylhex-3-yn-2-ol in the cage [13].

(b) Gives a formal representation of the free dimensions and contour of a cage. The scales of (a) and (b) differ.

(iv) Two kinds of fluorhectorite (FH) have been made by dry way sintering and flux melt reaction at 800 and 850°C [15]. One of these, FH-90, had an exchange capacity of 90 meq/100g and the other, FH-150, had an exchange capacity of 150 meq/100 g. They thus correspond respectively with a smectite and a vermiculite. The ethylene diammonium forms (ed-FH-90 and ed-FH-150) under static conditions at 50°C behaved [16] towards a selection of hydrocarbons as tabulated overleaf.

Ed-FH-90 appears able, under the static conditions employed, to differentiate between the n-, iso- and cyclo-paraffins and aromatics on the one hand and branched chain paraffins with quaternary carbon atoms on the other. Ed-FH-150 appears, inter alia, able to differentiate between benzene and other aromatics and between cyclopentane and cyclohexane.

The purpose of this section has been, by chosen examples, to demonstrate the growing variety of available sorbents and the potential richness of shape selective sorption in sorting out components of mixtures. It is assumed that this audience is already familiar with zeolite molecular sieves, and that no example of their great range of proven selectivities need be cited here.

	ed-FH90	ed-FH150
n-butane		
n-hexane		
n-octane		
iso-butane		
2,3-dimethyl butane	intercalated	intercalated
cyclopentane		
benzene		
cyclohexane		
toluene		
m-xylene		
mesitylene		not
neo-pentane	not	intercalated
2,2-dimethyl butane	intercalated	
2,2,4-trimethyl pentane		

THE FUTURE

I will conclude with some comments regarding the future of the science of porous crystals.

One can confidently expect further exploration and development of the porous aluminophosphates and the permanently expanded clay minerals. Other layer compounds exist which might be pillared and permanently expanded, such as the uranium micas, trititanates and graphitic oxide [17]. The further exploration of Werner compounds also seems well justified. Some of these are based on the octahedron, as also are the trititanates.

Of all types of porous crystal the zeolites have made much the greatest technological impact.
This position is likely to be maintained because of their variety and stability, their com-
bination of selective and shape-selective sorption, their activity as shape-selective
catalysts and catalyst carriers, and their behaviour also as selective and shape-selective
ion exchangers.   Zeolites are non-stoichiometric and can tolerate wide ranges of isomorphous
substitutions of tetrahedral framework atoms, T, by synthesis or by special techniques after
synthesis; and also, by cation exchange, of the extra-framework ions neutralising the frame-
work charge.   Both kinds of substitution can lead to miscibility gaps.   So far as framework
atoms, T, are concerned there is a need to determine quantitatively and as functions of tem-
perature what the miscibility limits are.   This is specially the case for replacements like

$$Al \rightleftharpoons Fe, Cr, B \text{ etc}$$

and requires quantitative identification and measurement of framework T atoms and T atoms in
detrital extra-framework material.   Ideally, as in the much studied area of the felspars,[18]
binodal phase separation curves for isomorphous replacements would be sought.   A number of
examples have been observed where phase separation in zeolites involves only cation migration.
In these systems, because of the favourably high mobility of cations within the crystals, it
should be possible to measure both binodal and spinodal phase separation boundaries [18].

Zeolites are solid electrolytes and developments based upon this, such as ion selective mem-
brane electrodes, have so far received only limited attention [19].   The cations in zeolites
are normally distributed, along with cation vacancies, among a number of sub-lattices [20].
These distributions at equilibrium require much more quantitative study in order to establish
equilibrium constants as functions of temperature, and such derived thermodynamic quantities
as energies and entropies of transfer between sub-lattices.   Information is also limited as
to the extent to which these distribution equilibria are changed in the presence of varying
amounts of a given type of guest molecule.

Because of the almost unlimited numbers of zeolite or porosil structures that can be built as
models, as compared with the present harvest, one may expect the future synthesis of many
more novel structures, provided sufficient effort and chemical ingenuity is deployed.   Such
creative chemistry is stimulated not only by its scientific interest but also by potential
industrial rewards.   In selective catalysis and sorption zeolites have already created some-
thing of a revolution, and one anticipates zeolite-based catalysts of greater and greater
specificity approaching or reaching the "lock and key" action of enzymes, as the range of
catalysts is extended, using zeolites and other porous crystals already made or still to be
synthesised.

Finally, I suggest that there seems no reason why the thermal gradient hydrothermal method of
growing massive synthetic quartz crystals and also artificial gems [21] should not be equally
applicable to growing massive crystals of ZSM-5 or silicalite I and other zeolites or poro-
sils.   In this event it might be possible to cut practical membranes capable of direct
molecule sieving.

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