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EVIDENCE FROM COMPUTATIONAL CHEMISTRY FOR THE EXISTENCE OF A NEW ZEOLITIC CATALYST

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On the basis of both computed energy and a specific crystallographic strategy recently formulated (Akporiaye and Price, submitted 1988 [12]) we advance reasons for the existence of a new type of zeolitic structure related to zeolite ECR-1 (Leonowicz and Vaughan [4]). Although ECR-1 and the new structure have identical projections along one axis, the new structure differs from the former in that it cannot be regarded as made up of recurrent, integrown strips of mordenite and mazzite. Rather it consists of two different structural components. We also predict the corresponding X-ray diffractograms; and show that several other types of related zeolitic structures are expected to exist.

Zeolites are unusually versatile catalysts [1–3]. They possess sharply defined pore-size distributions, high and adjustable acidity, very high surface areas (typically 600 m^2g^{-1}) the majority of which are accessible through apertures of well-defined dimensions, and good thermal stability. Moreover, transition metal- and other ions can be 'placed' in well-defined, catalytically active sites within the cages and channels of the zeolite. Since different catalytic properties are displayed by zeolites of different structure, and since the scope for catalyst design is very considerable in this class of microporous solid, the possibility of producing a new zeolitic structure is of considerable interest to the catalyst scientist.

Recently Leonowicz and Vaughan [4] identified a new zeolite, ECR-1, synthesized at the *E*xxon *C*entral *R*esearch Station, New Jersey. The framework structure, projected along the *a* crystallographic axis is shown in fig. 1, from which it can be seen that this zeolite may be regarded as being made up of coherent, recurrent intergrowths, at the sub-unit-cell level [5], of strips of the well-known zeolitic minerals mordenite and mazzite. Although no single-crystal studies have yet been possible, the broad structural outlines of ECR-1 are well represented by the model shown in fig. 1 for a variety of spectroscopic and other, notably high-resolution electron microscopic, reasons.

There is, however, doubt concerning the mode of connection between the strips of mordenite and mazzite from which ECR-1 is pictured to be built up. Are these strips connected by the so-called 5, 5 – sequence (ECR-1A) shown in fig. 2(a), or by the 4, 6 – sequence (ECR-1B) in fig. 2(b)? It is conceivable that this ambiguity

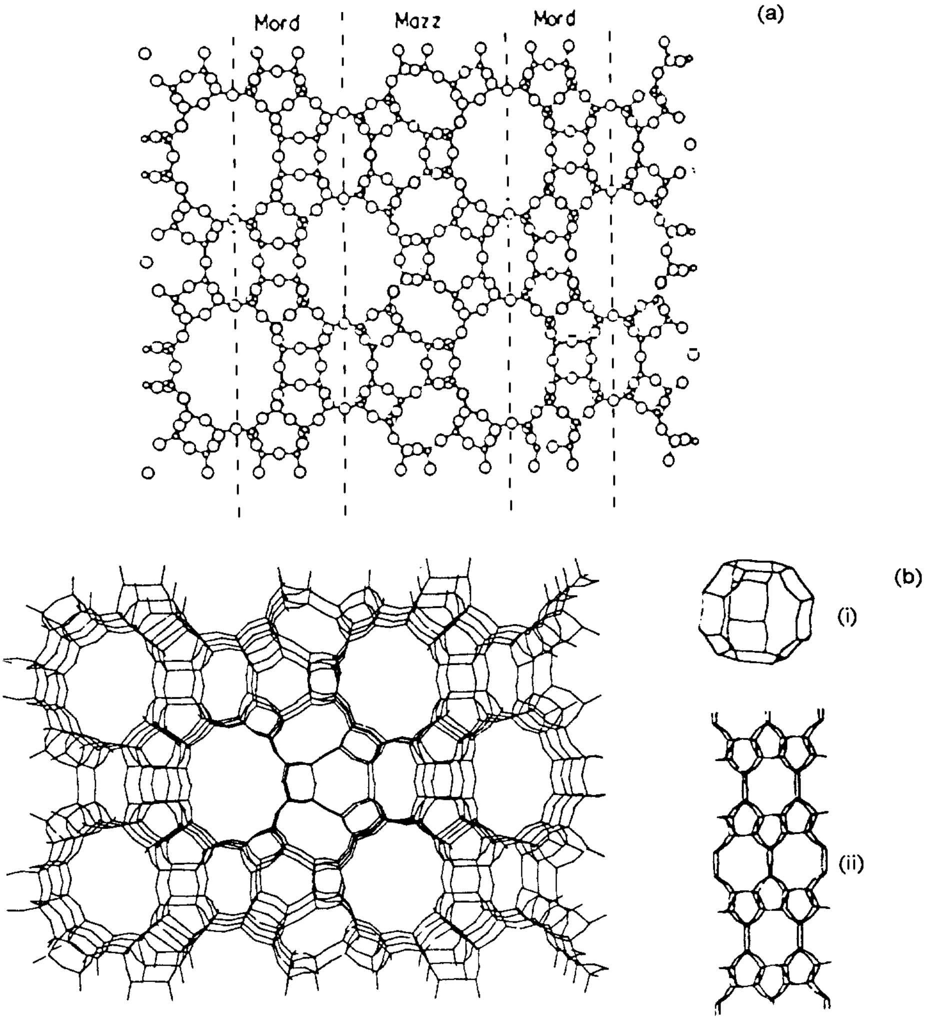

Fig. 1. (a) Projection of ECR-1A along the a-axis showing the component strips of mordenite and mazzite; large spheres denote oxygen atoms, small spheres are T-atoms (Si and Al). (b) Perspective view of the ECR-1A framework. Inset (i) shows the gmelinite cage as observed in mazzite, inset (ii) shows a layer of the mordenite structure.

may be resolved by high-resolution X-ray or neutron Rietveld analysis of the powder diffraction data [6,7], or when it becomes possible to record 1000 keV high-resolution electron microscopic images [8] down the 010 zone axis.

As the detailed catalytic and adsorptive properties of the ECR-1 are likely to be different for the two structural possibilities shown in figs. 2(a) and (b), we undertook a computational study of the siliceous (i.e. pure SiO_2 polymorphic) forms of figs. 2(a) and 2(b) using the core model procedures developed by Catlow

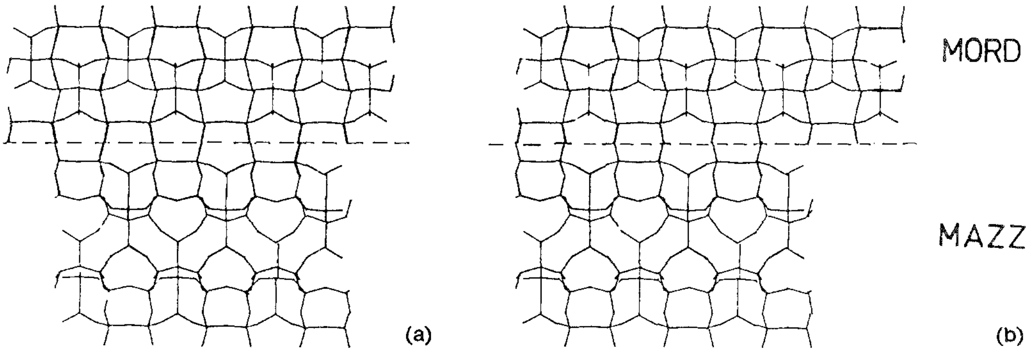

Fig. 2. Two alternative modes of connection between mordenite and mazzite strips, (a) via 5, 5 – rings and (b) via 4, 6 – rings.

et al. [9–11] for energy minimization of such solids. Briefly, a fully ionic, interatomic potential model is used to describe the interaction between the ions that constitute the SiO_2 framework. Using empirically derived parameters for silicates [11], the energy of the crystal is minimised with respect to all structural parameters, predicting the lattice energy of the minimum energy structure. A cut-off radius of 13.27 Å was used in these calculations. Our results showed the difference in lattice energy to be 0.02 eV per SiO_2-unit in favour of ECR-1A, a negligible amount.

However, using the general strategy of Akporiaye and Price [12]–who have shown how, in general, the structures of zeolites may be conceptually broken down into, or assembled from, component layers–we were able to identify a number of new types of zeolite structures, all with the same ECR-1 projection.

Figure 3(a) shows ten of the possible structures with the ECR-1A projection. The three-dimensional arrangements of atoms in the layers varies as indicated by the arrows. Arrowheads mark the elevation of T atoms above the level of atoms connected by unmarked lines. The resulting 'corrugation' of the layer in ECR-1A is shown in fig. 3(b). Complete structures may be generated from the component layers by mirror or translation operations.

A method developed by Akporiaye and Price [13] confirmed structure *C* in fig. 3(a) to be the most appropriate for investigation as a possible new structure. For convenience we designate this structure DF (*D*avy *F*araday). It may be regarded as a recurrent intergrowth of two separate structures (see fig. 4) neither of which, to our knowledge, is known as a pure phase. We note that there are:
(a) strings of cancrinite cages sharing 6 – rings (inset (i), fig. 4) and
(b) strings of connected 4 – , 5 – and 6 – rings (inset (ii), fig. 4).

It is noteworthy that (a) has previously been described by Barrer and Villiger [4] and (b) by Sherman and Bennett [15] in the enumeration of alternative

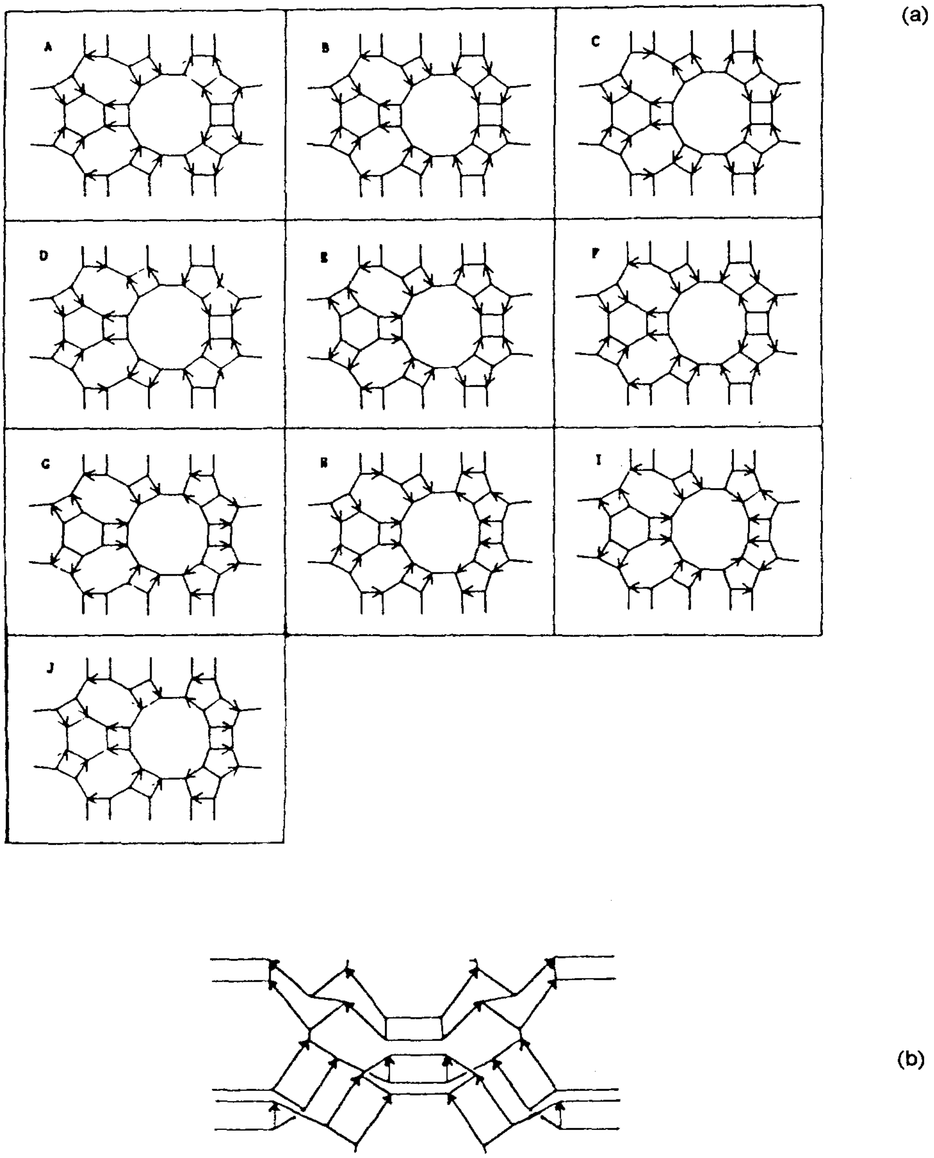

Fig. 3. Ten possible structures with the ECR-1 projection, generally the methodology of Akporiaye and Price. Arrowheads indicate T-atoms lying above the plane of atoms with unmarked bonds. (b) Three-dimensional representation of alternative structure A (ECR-1A) from fig. 3(a).

structure types of synthetic zeolite L and mordenite respectively. In contrast, ECR-1 consists of strings of connected gmelinite cages (as in mazzite) and mordenite strips. These are shown as insets in fig. 1(b). The two fragments isolated from the structures of ECR-1A and DF shown in figs. 5(a) and (b) highlight the differences in framework geometry along the short axis.

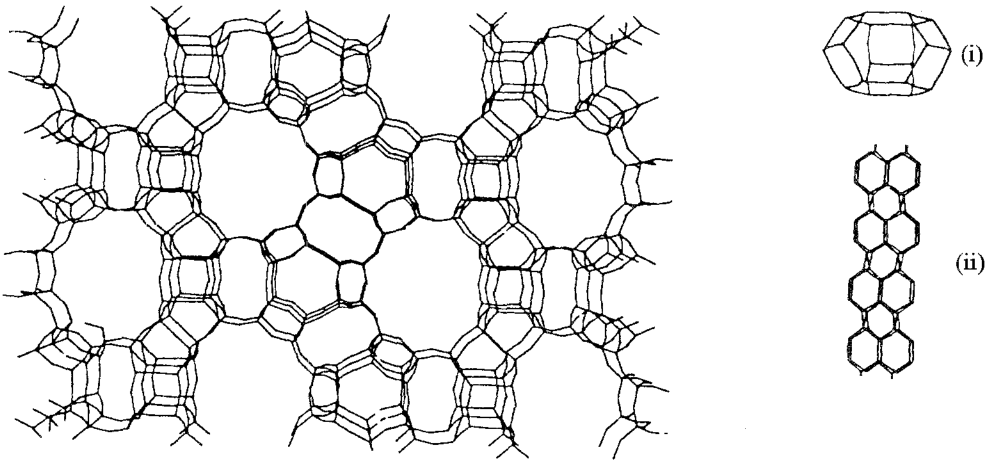

Fig. 4. Perspective view of the framework of DF. Inset (i) shows the cancrinite cage and inset (ii) shows the layer of 4 – , 5 – and 6 – rings which is found in DF.

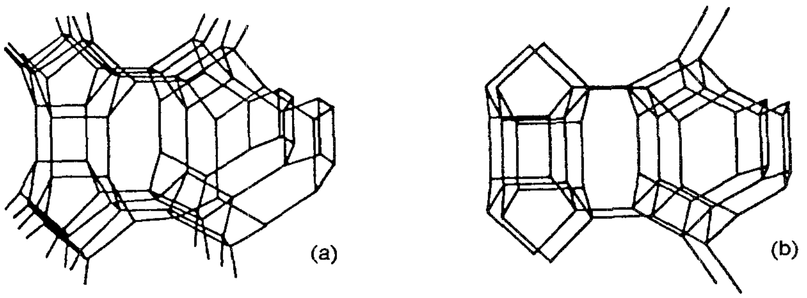

Fig. 5. Fragments isolated from perspective views of ECR-1A (a) and DF (b).

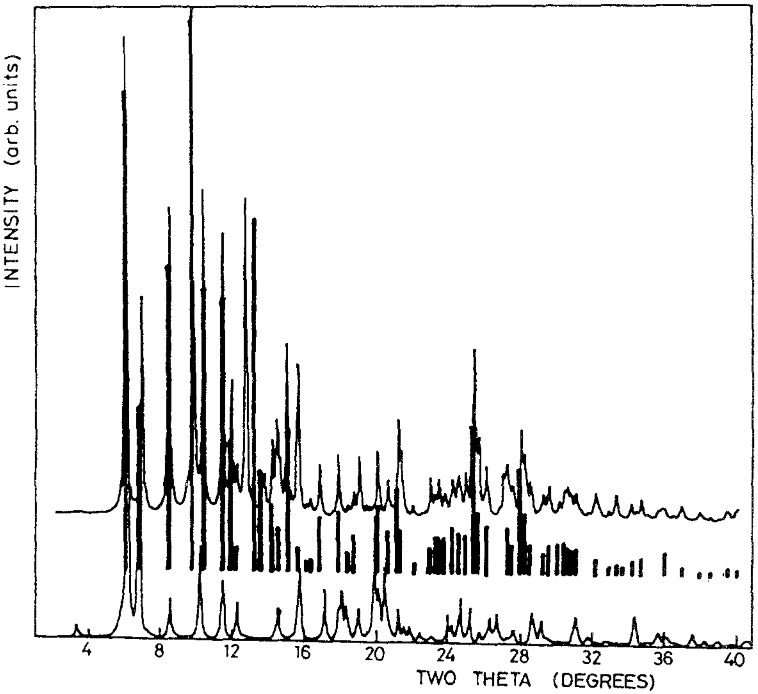

Fig. 6. Calculated diffraction patterns for siliceous forms of (a) DF, (b) ECR-1A and (c) ECR-1B.

Table 1
Calculated cell constants and atom positions for DF
Space group: *Pmma* (no. 51)
Cell constants: $a = 17.2752$, $b = 5.2003$, $c = 25.7146$ Å

Atom	Position	X	Y	Z
T1	4j	0.5138	0.5000	0.1393
T2	4j	0.4286	0.5000	0.2454
T3	4j	0.3400	0.5000	0.9284
T4	4j	0.0670	0.5000	0.3663
T5	4j	0.0607	0.5000	0.5469
T6	4i	0.3405	0.0000	0.2110
T7	4i	0.4252	0.0000	0.1053
T8	4i	0.3400	0.0000	0.9968
T9	4i	0.1592	0.0000	0.4004
T10	4i	0.1588	0.0000	0.5235
01	4j	0.4919	0.5000	0.1998
02	81	0.4737	0.7489	0.1167
03	4j	0.5989	0.5000	0.1171
04	81	0.3796	0.7497	0.2338
05	4j	0.4482	0.5000	0.3054
06	81	0.3520	0.7491	0.9629
07	2f	0.7500	0.5000	0.0844
08	81	0.1159	0.7501	0.3803
09	4j	0.9933	0.5000	0.4031
010	81	0.1134	0.7497	0.5416
011	2d	0.0000	0.5000	0.5000
012	4i	0.3664	0.0000	0.1522
013	4i	0.3871	0.0000	0.0495
014	2f	0.7500	0.0000	0.7838
015	2f	0.7500	0.0000	0.9930
016	4i	0.1552	0.0000	0.4619
017	2f	0.7500	0.0000	0.6109
018	2f	0.7500	0.0000	0.4650

We compute the total energy of the siliceous form of DF to be 0.16 eV per SiO_2 group lower (i.e. more stable) than that of ECR-1A. DF is, therefore, predicted to exist on energetic grounds.

We have not attempted to synthesize this theoretically possible new zeolitic catalyst DF. It is conceivable that it has already been prepared. To assist in such a retrospective 'search', we have computed the powder diffractogram of the sileceous form of DF (fig. 6) along with the corresponding diffractograms of siliceous ECR-1A and ECR-1B. These diffractograms are suitable for comparison with the H^+-form derived from the heat-treated NH_4^+-form of the respective zeolites even for finite values of Si/Al ratios. Predicted unit cell constants and atomic positions for DF in the space group *Pmma* are given in table 1.

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