

## Synthesis and Proposed Framework Topology of Zeolite SUZ-4

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Crystalline SUZ-4, with anhydrous composition  $K_5Al_5Si_{31}O_{72}$ , is hydrothermally synthesized in a reaction mixture of  $SiO_2$ ,  $Al_2O_3$ , KOH, tetraethylammonium hydroxide and quinuclidine; its proposed framework topology is related to zeolites ferrierite and ZSM-57 and contains straight channels having apertures defined by rings of ten (Si, Al)-O species; a novel cage may serve as the site for non-exchangeable potassium ions.

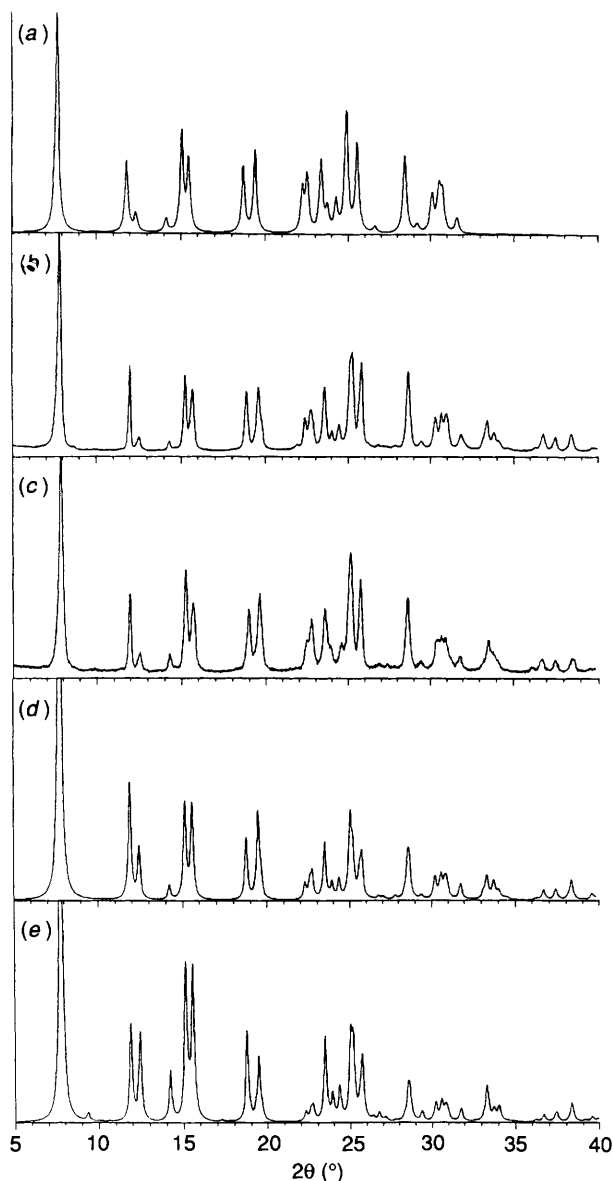
Zeolites are crystalline, microporous molecular sieves having three-dimensional framework structures. The framework consists of silicon, aluminium and oxygen, for which the name aluminosilicate is used. Zeolites may contain cavities and/or channels occupied by ions and water molecules.

SUZ-4 is a new synthetic aluminosilicate recently patented by British Petroleum Co.<sup>1</sup> A comparison of the published X-ray diffraction (XRD) powder data for SUZ-4 with those of known zeolites indicated that this zeolite may be related to ferrierite. R. Gramlich-Meier has shown<sup>2</sup> that ferrierite contains a chain of T-O-T linkages found in the mineral wollastonite (T is a tetrahedrally-coordinated atom, either Si or Al). When this chain is linked together in a variety of ways, six structurally-related framework topologies (Gramlich-Meier models **5a-5f**) are produced. Ferrierite corresponds to

model **5d**. Zeolite ZSM-57, reported four years later, has subsequently been shown to have a topology that corresponds to model **5f**.<sup>3</sup> A comparison of the observed XRD powder pattern for SUZ-4 with the simulated (computed) XRD powder patterns for the remaining four hypothetical models revealed a close match with model **5b**.

Crystals of SUZ-4 were synthesized hydrothermally by using Ludox AS40 (40%  $SiO_2$ , DuPont), sodium aluminate (43.3%  $Al_2O_3$ , 32.2%  $Na_2O$ , Nalco), potassium hydroxide (KOH, 45% solution), tetraethylammonium hydroxide (TEAOH, 40% solution, SACHEM) and quinuclidine (Aldrich).

In a typical preparation, 30 g of TEAOH were added, with stirring, to a solution of 7.4 g sodium aluminate, 22.7 g KOH and 190 g water. To this mixture was added 9.1 g quinuclidine,

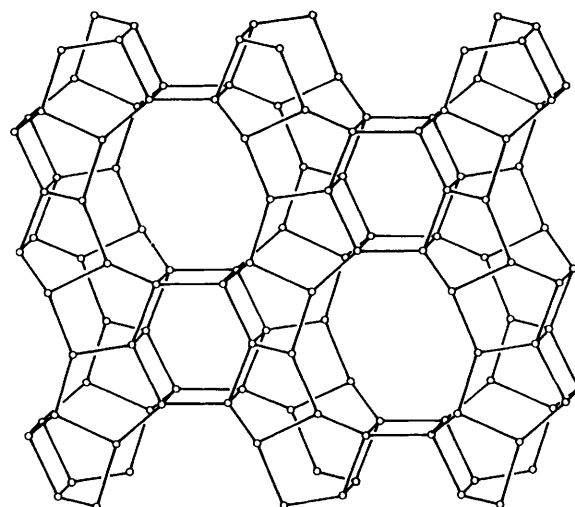


**Fig. 1** Observed XRD powder patterns of SUZ-4 and calculated patterns of the hypothetical model, based on Cu-K $\alpha$  radiation. (a) Calcined SUZ-4 from ref. 1(a); (b) calcined SUZ-4; (c) NH $_4^+$ -exchanged, calcined SUZ-4; (d) proposed model, framework plus K $^+$  at (0,0,0); (e) proposed model, framework only. Patterns (a), (d) and (e) are simulated; patterns (b) and (c) are observed.

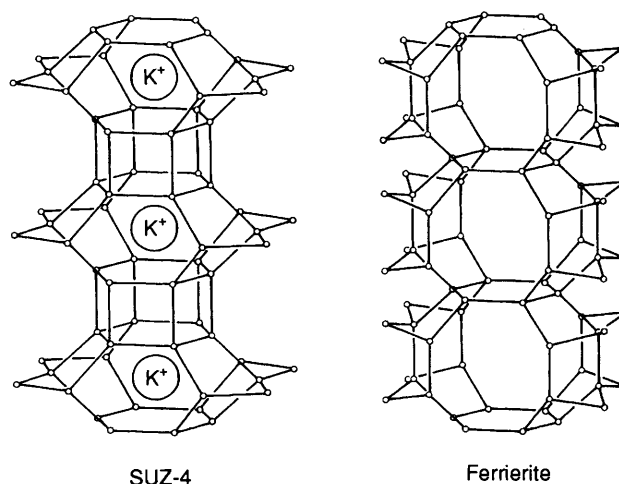
followed by 100 g Ludox. The slurry was transferred to a stainless steel autoclave and crystallized at 150 °C with agitation, 250 rpm, for 48 h. The solid product was washed with water and dried at 120 °C. Scanning electron microscopy (SEM) of the calcined material shows it to be of fibrous morphology, with bundles of fibres up to 1  $\mu$ m in length. The chemical composition of the as-synthesized zeolite, expressed on a per unit cell basis, was K $_5$ Al $_5$ Si $_{31}$ O $_{72}$ .

A portion of the as-synthesized material was calcined in air at 540 °C for 24 h. This calcined product had the XRD powder pattern shown in Fig. 1(b). Comparison of this pattern with that reported in ref. 1(a) [Fig. 1(a)] indicated that it was pure SUZ-4.

A 10 g portion of the calcined zeolite was treated with four 1 h contacts of 10% NH $_4$ Cl solution. It was then filtered, water washed, dried at 120 °C and calcined at 540 °C for 16 h. The K content reduced to 3.3%. The XRD pattern of this treated, calcined product is shown in Fig. 1(c). Although the potas-



**Fig. 2** SUZ-4 framework viewed along [001] direction



**Fig. 3** Columns along the unit cell  $c$ -axis in SUZ-4 and ferrierite. The proposed location of the non-exchangeable potassium ion in SUZ-4 is shown.

sium content decreased somewhat, the XRD powder pattern changed very little.

Characterization of this product by X-ray crystallography $^\dagger$  has provided strong support for the proposed model. The proposed framework topology of SUZ-4, shown in Figs. 2 and 3, consists of five-, six-, eight- and ten-membered rings; four-membered rings are only present as part of double six-membered rings. The  $ab$ -projection is identical to the  $ab$ -projection of the mineral ferrierite. Both SUZ-4 and ferrierite have a  $c$ -axis repeat of *ca.* 7.5 Å, and both have the

$^\dagger$  Crystal data for calcined SUZ-4: K $_5$ Al $_5$ Si $_{31}$ O $_{72}$ , orthorhombic,  $Cmmm$  (No. 65),  $a = 18.915(9)$ ,  $b = 14.238(6)$ ,  $c = 7.442(4)$  Å,  $Z = 1$ . The unit cell parameters correspond to refined values, corrected for zero-point error, $^4$  that are based on synchrotron X-ray diffraction data of the calcined sample prior to ammonium exchange.

The proposed model for the framework topology was subjected to a constrained distance and angle least-squares (DLS $^5$ ) refinement. In these refinements the prescribed T-O, O...O, and T...T distances were optimized at 1.62, 2.65 and 3.09 Å, respectively, using relative weights of 2.0, 1.0 and 0.1. The unit cell parameters were held fixed. The final values of  $R$  and  $\sigma$  were 0.0087 and 0.0363, respectively. The refined atomic coordinates are listed in Table 1. The corresponding computed pattern for just the framework is shown in Fig. 1(e).

The indexed diffraction data used to refine the unit cell parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

**Table 1** Final DLS atomic coordinates for the proposed model of SUZ-4

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>
T(1)	16r	0.0793	0.1982	0.2864
T(2)	8o	0.1445	0.0	0.2860
T(3)	4g	0.2677	0.0	0.0
T(4)	8p	0.1724	0.2964	0.0
O(1)	8n	0.0	0.2219	0.2211
O(2)	16r	0.0992	0.0920	0.2316
O(3)	8o	0.2188	0.0	0.1780
O(4)	4e	0.25	0.25	0.0
O(5)	8p	0.3187	0.0911	0.0
O(6)	16r	0.1316	0.2685	0.1804
O(7)	4h	0.1596	0.0	0.5
O(8)	8q	0.0869	0.2134	0.5

same type of infinite chains that occurs in the mineral wollastonite.

The major difference between SUZ-4 and ferrierite is the alignment of these chains along the *c*-axis. This difference results in SUZ-4 having double six-membered rings between small cages and ferrierite having single six-membered rings between large cages, as shown in Fig. 3. The relationship between SUZ-4 and ferrierite, involving six-membered rings and cages, has a structural counterpart with two known zeolites in the hexagonal system, namely erionite and TMA-E(AB). The ten-membered ring channels in SUZ-4 are straight. The minimum and maximum dimensions of the ten-membered ring are 4.6 and 5.2 Å, respectively, which are similar to those in ferrierite (4.2 and 5.4 Å). (The computed pore openings are based on an oxygen radius of 1.35 Å.)

The computed XRD pattern for the framework, shown in Fig. 1(e), compares favourably with the observed patterns

[Figs. 1(b) and 1(c)]. Recognizing that the intensity differences may be due to the presence of potassium in the structure, site location of potassium was explored. The as-synthesized form of SUZ-4 contains potassium at the 5.7 wt% level. When subjected to an ammonium exchange and calcination, it reduced to only 3.3%, indicating that some of the potassium ions are probably locked in a small cage. Three sites (0,0,0; 0,0,1/2 and 1/4,1/4,1/2) are possible candidates for this ion. Site S1 (0,0,0) is the centre of the small cage; site S2 (0,0,1/2) is the centre of a double six-membered ring; and site S3 (1/4,1/4,1/2) corresponds to the centre of a non-planar, modified, double eight-membered ring. If fully occupied by potassium, sites S1 and S2 would each have two potassium ions per unit cell. Site S3 corresponds to four potassium ions per unit cell. Trial computations of XRD powder patterns with potassium in each of these three sites indicated that site S1 was the preferred site. This site is shown in Fig. 3. The corresponding XRD powder pattern is shown in Fig. 1(d), and it is this pattern that significantly increased our confidence in the model for SUZ-4.

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