

# CIT-5: a high-silica zeolite with 14-ring pores

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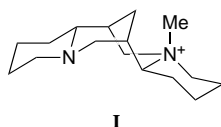
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The synthesis and structure of a new zeolite, CIT-5 (California Institute of Technology Number Five), is described, which possesses one-dimensional pores comprised of 14 T-atoms (tetrahedrally coordinated silicon or aluminium atoms).

Zeolites with pores comprised of larger than 12 T-atoms (extra-large pores) are much in demand<sup>1–4</sup> and have been so for many years.<sup>4–7</sup> The reason for this is the desire to perform catalysis/adsorption on molecules > 8 Å in size.

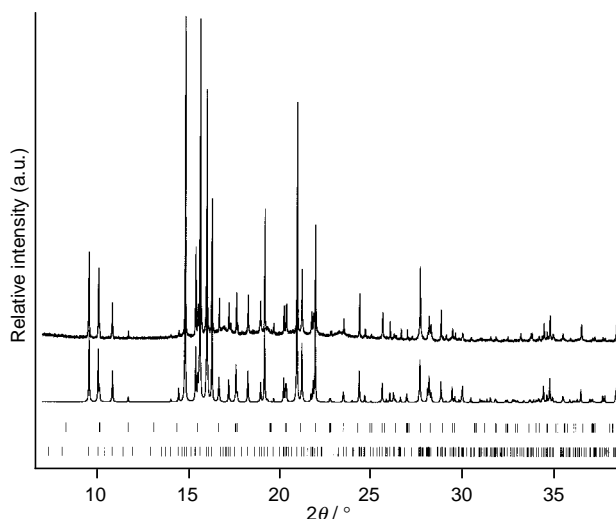
The first molecular sieve with extra-large pores was VPI-5 that is an aluminophosphate material with 18-ring pores.<sup>8</sup> Subsequently, other phosphate-based extra-large pore materials have been reported, e.g. cloverite.<sup>2</sup> All of the phosphate-based molecular sieves lack the desired properties of combined high acidity and thermal/hydrothermal stability and thus limit the practical potential. Recently, the first extra-large pore zeolite, UTD-1, was reported and shown to possess good acidity and thermal/hydrothermal stability.<sup>9,10</sup> Additionally, there have been numerous disclosures of ordered, aluminosilicate mesoporous materials with pore sizes of 20–100 Å.<sup>11,12</sup> Because the inorganic portions of the mesoporous materials are not crystalline, they lack the acidity and thermal/hydrothermal stability of high-silica zeolites.<sup>13</sup>

Here, we report a new extra-large pore zeolite denoted CIT-5. CIT-5 is synthesized under hydrothermal conditions. A reaction mixture of composition 0.2 ROH:0.1 LiOH:0.02 Al<sub>2</sub>O<sub>3</sub>:1 SiO<sub>2</sub>:40 H<sub>2</sub>O is heated to 175 °C at autogenous pressure for ca. 12 d in order to produce CIT-5. In the absence of aluminium, pure-silica CIT-5 can be prepared in 5 d. The organic structure-directing agent (SDA), R, is *N*(16)-methylsparteinium **I** and is prepared as previously reported.<sup>14</sup> In the absence of lithium, **I** can form pure-silica or borosilicate SSZ-24.<sup>13,14</sup> Thus, the key to the successful preparation of CIT-5 is both the SDA **I** and the inclusion of lithium. Further synthetic details are forthcoming.<sup>15</sup>



Indexation<sup>16</sup> of the synchrotron powder X-ray diffraction (SPXRD) data from the pure-silica sample of CIT-5 revealed the presence of a small amount of an impurity phase together with the predominant CIT-5 phase. The CIT-5 material indexed in the orthorhombic crystal class with refined lattice constants  $a = 13.694(2)$ ,  $b = 5.0213(5)$ , and  $c = 25.4970(3)$  Å ( $U = 1753.2$  Å<sup>3</sup>). The lattice constants for the impurity hexagonal phase were found to be  $a = 13.63$  and  $c = 8.30$  Å. The unit cell parameters and scanning electron micrographs helped to identify the impurity phase as SSZ-24 (International Zeolite Association Code AFI).<sup>17</sup> Systematic absences for the orthorhombic CIT-5 phase indicate body-centering consistent with six possible space groups.

The starting model for Rietveld refinement of CIT-5 was obtained by an iterative process of model building, distance-



**Fig. 1** Experimental (top) and simulated (bottom) powder XRD data of CIT-5,  $\lambda = 1.20028(5)$  Å. The upper tick marks represent peak positions for the impurity phase, SSZ-24, while the bottom set of tick marks represents peak positions for CIT-5.

least squares (DLS)<sup>18</sup> refinement of the atomic positions for the model, and comparison of the simulated powder X-ray pattern (CERIUS<sup>19</sup>) to the experimental pattern. The model with the closest match between the simulated X-ray powder pattern and the experimental XRD was found to have maximal topological symmetry of space group *Imma* (no. 74, standard setting) (consistent with the systematic absences).

A two phase Rietveld refinement<sup>20</sup> was carried out using the structural parameters previously reported for the SSZ-24 impurity phase.<sup>13</sup> The background, scale factor and zero shift were refined, followed by refinement of the lattice parameters, peak shape function parameters and atomic positions for both

**Table 1** Crystallographic and refinement data

Space group	<i>Imma</i> (no. 74)
$a/\text{Å}$	13.6947(2)
$b/\text{Å}$	5.0213(5)
$c/\text{Å}$	25.4970(3)
$\lambda/\text{Å}$	1.20028(5)
$T/\text{K}$	298
Profile range/°	5–42.2
Step scan increment/°	0.005
No. observation	7440
No. structural parameters	55
No. profile parameters refined	5
No. background parameters	20
$R_{\text{wp}}$ (%)	11.43
$R_{\text{p}}$ (%)	8.75
$DW_{\text{d}}$ <sup>a</sup>	0.040
Reduced $\chi^2$	6.898

<sup>a</sup> No serial correlation in fit at 90% confidence for  $1.950 < DW_{\text{d}} < 2.050$ .

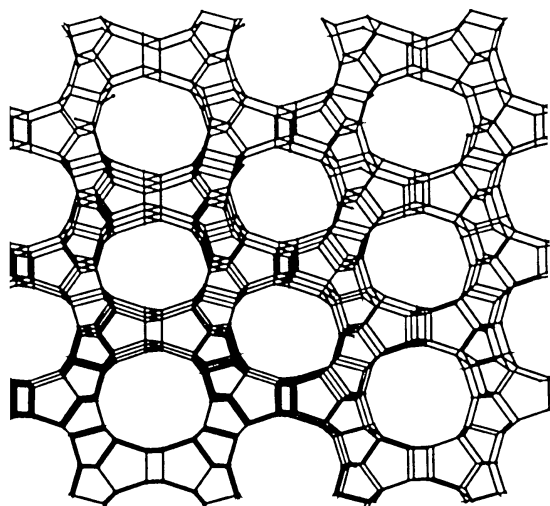


Fig. 2 The [010] projection of CIT-5 showing the 14MR pores

CIT-5 and SSZ-24. Isotropic thermal parameters for the CIT-5 phase were also refined. The phase fraction refinement indicated *ca.* 4% SSZ-24 impurity. The low values of the residuals ( $R_p = 8.7\%$  and  $R_{wp} = 11.4\%$ ) indicate close agreement between the calculated intensities from the refinement and the experimentally observed intensities (Fig. 1). Further details of the refinement results can be found in Table 1.

The structure of CIT-5 viewed down the *b*-axis is shown in Fig. 2 and is composed of one-dimensional, extra-large pores of nearly circular cross section (center of oxygen to center of oxygen distance  $10.0 \times 9.9 \text{ \AA}$ ) circumscribed by 14-T-atom-membered rings (14MRs). The asymmetric unit contains 5 T-atoms and 8 oxygens resulting in a unit cell content of  $[\text{Si}_{32}\text{O}_{64}]$ , a framework density (FD) of 18.3 T-atoms/1000  $\text{\AA}^3$ , and a density of  $1.821 \text{ g cm}^{-3}$ . Table 2 contains the final atomic positional parameters and isotropic temperature factors obtained from the Rietveld refinement.

Comparison of the simulated, experimental and image processed experimental high resolution transmission electron micrographs (HRTEM) of CIT-5 viewed down the pores ([010] projection) are shown in Fig. 3, and confirm the topology of the structure. The primary building unit of CIT-5 is a zigzag ladder of four-membered rings (4MRs) with pendant five-membered rings (5MRs). These units are interconnected through single zigzag chains to form the body centered structure shown in Fig. 2. Electron diffraction patterns of CIT-5 show no signs of streaking indicating that the structure is not faulted or disordered.

Thermogravimetry showed an 11.2 mass% loss from **I** by  $700 \text{ }^\circ\text{C}$  (in air). This amount of organic gives a pore volume of

Table 2 Refined atomic positional parameters in space group *Imma* (No. 74) and isotropic thermal parameters (eds. in parentheses)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/\text{\AA}^2$
Si(1)	0.1160(6)	0.2500	0.0317(2)	0.042(4)
Si(2)	0.0000	0.7500	0.2788(6)	0.082(6)
Si(3)	0.2820(5)	0.7500	0.1887(3)	0.050(4)
Si(4)	0.0000	0.2500	0.2177(4)	0.020(4)
Si(5)	0.1936(6)	0.2500	0.1479(4)	0.041(3)
O(6)	0.0000	0.2500	0.0512(6)	0.049(6)
O(7)	0.0853(9)	0.2500	0.1737(4)	0.015(6)
O(8)	0.0000	0.5776(31)	0.2309(5)	0.110(9)
O(9)	0.1303(9)	0.0000	0.0000	0.539(9)
O(10)	0.1896(6)	0.2500	0.0909(4)	0.060(4)
O(11)	0.2500	0.7500	0.2500	0.086(11)
O(12)	0.0913(11)	0.7500	0.3099(5)	0.047(6)
O(13)	0.2640(7)	0.4474(22)	0.1665(4)	0.070(6)

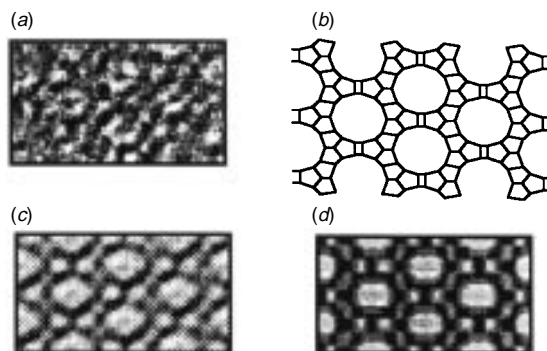


Fig. 3 High-resolution transmission electron micrographs (HRTEM): (a) experimental, (b) [010] projection of CIT-5, (c) processed experimental image and simulated image (d). Samples for HRTEM were prepared by microtomy and images were recorded using a Phillips 430 electron microscope operating at 200 kV.

$0.128 \text{ ml g}^{-1}$  and is consistent with the pore volume calculated from the structure ( $0.135 \text{ ml g}^{-1}$ ). While CIT-5 contains extra-large 14MR pores, temperature dependent powder XRD studies show that it has very high thermal and hydrothermal stability. The calcined material remains crystalline to over  $900 \text{ }^\circ\text{C}$ , both under pure nitrogen atmosphere and under nitrogen atmosphere containing *ca.* 23 Torr  $\text{H}_2\text{O}$ .

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## Footnotes and References

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