# Zeolite-β grown epitaxially on SSZ-31 nanofibers

**Sankar Nair,[a] Luis A. Villaescusa,[b] Miguel A. Camblor*[b] and Michael Tsapatsis*[a]**

[a] *Department of Chemical Engineering, University of Massachusetts, Amherst MA 01003, USA. E-mail: tsapatsi@ecs.umass.edu*

[b] *Instituto de Tecnología Química (CSIC-UPV), Universidad Politécnica de Valencia, Avda. Los Naranjos s/n, 46071 Valencia, Spain. E-mail: macamblo@itq.upv.es*

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**The synthesis and characterization of an epitaxial growth of zeolite β on SSZ-31 nanofibers is described, and a structural model of the interface between the two zeolites is proposed.**

Zeolite crystals in the form of nanofibers have several potential catalytic applications, owing to the short diffusion lengths across these fibers and their low resistance to fluid flow (low pressure drop), as well as other advanced materials applications owing to the possibility of incorporating them in membrane, sensor or electronic devices. A few zeolites with one-dimensional (1-D) pore systems are known to crystallize in a needle-like morphology[1–3] with the channels running along the long axis of the particles. This raises the possibility of epitaxially growing other zeolitic structures on nanofibers of such 1-D pore zeolites. We report here, the first such epitaxial process, involving the growth of zeolite-β on nanofibers of the 1-D zeolite SSZ-31, and we propose a structural model for the interface between the two zeolites.

Zeolite-β is an industrially important large-pore material, widely used in catalytic and adsorption processes.[4,5] Previous syntheses of zeolite-β resulted in equiaxed particles that contain both the β polymorphs A and B. In this study, zeolite-β was synthesized as pure silica polymorph using 1,3,3,6,6-pentamethyl-6-azoniumbicyclo[3.2.1]octane cation as the organic structure-directing agent (SDA). This cation was synthesized by quaternization of the parent amine with an excess of MeI in $CCl_3H$, and was used in hydroxide form after anion exchange of the iodide.

For the zeolite synthesis, tetraethylorthosilicate (21.89 g) was hydrolysed in 35.02 g of an aqueous solution of the SDA in hydroxide form (1.49 mmol $g^{-1}$). The mixture was stirred, allowing evaporation of the ethanol produced in the hydrolysis. Further stirring for 3 h at room temperature allowed the evaporation of a total mass of 22.69 g (ethanol plus water). Then, HF (2.18 g, 48% aqueous solution) was added and the mixture was shaken till homogeneous. Hydrothermal crystallization of this mixture (final composition $SiO_2:0.5\ C_{12}H_{24}NOH:0.5\ HF:9.9\ H_2O$) in rotating (60 rpm) Teflon-lined stainless steel autoclaves at 150 °C for 20 days produced a crystalline solid with an XRD pattern similar to that of zeolite-β.[6,7]

However, there were several facts suggesting that this material was not identical to zeolite-β and that it could also be related to zeolite SSZ-31. First, the XRD pattern shows some differences with the pattern of zeolite-β and some similarities with that of SSZ-31[3,8]. For instance, the shape of the first broad peak at low angle is more like that of the second peak in SSZ-31 rather than the first peak in zeolite-β. Also, the separation of the two main peaks in the range $2\theta$ 20–22.5° of 1.20° is closer to that in SSZ-31 (1.28°) than in β (1.08°). Furthermore, the adsorption capacity of this material (0.13 $cm^3\ g^{-1}$) calculated from the $N_2$ adsorption isotherm using the *t*-plot method, is intermediate between those of zeolites β (0.19 $cm^3\ g^{-1}$) and SSZ-31 (0.08 $cm^3\ g^{-1}$). Interestingly, when the final water:silica ratio in the above synthesis mixture composition was increased to 15, SSZ-31 was obtained (when the ratio was decreased to 7.5, ITQ-3[9] was the crystallization product). All these suggested that the synthesized solid could actually be an intergrowth of zeolites β and SSZ-31.

To characterize the synthesized crystals, transmission electron microscopy was performed with a JEOL 3010 microscope operating at 300 kV. A low-resolution TEM image shows that a significant number of crystals are nanofibers of length 1–2 μm, with radial outgrowths *ca.* 20 nm in radius [Fig. 1(a)]. A few fibers of length up to 5 μm have also been observed. A high-resolution TEM image [Fig. 1(b)] from the center of such a crystallite reveals that a nanofiber of zeolite SSZ-31 forms a 'backbone' (running along the centerline of the nanofiber) for epitaxial growth of zeolite-β. This is further corroborated by the presence of SSZ-31 nanofibers free of zeolite-β outgrowths. Complete channels of β (polymorph B) lie immediately above the β/SSZ-31 interface. Two SSZ-31 channels are observed, apparently running parallel to the second channel direction of zeolite-β. These observations suggest that the β/SSZ-31 interface contains composite 12-membered channels constructed from β and SSZ-31 'half-channels'. The SSZ-31 'backbone' is observed to be always three unit cells thick.

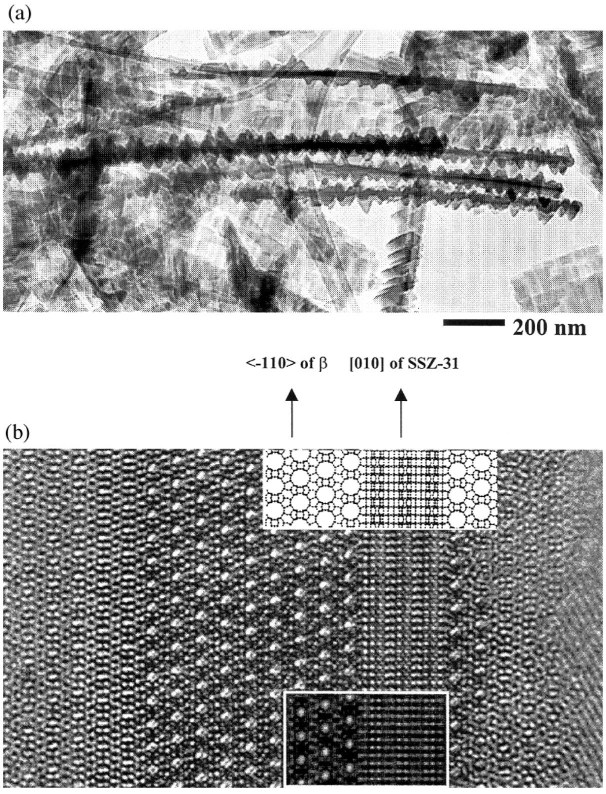

**Fig. 1** (a) TEM image of synthesized crystals showing SSZ-31 nanofibers with epitaxial outgrowths of zeolite-β; (b) high-resolution TEM image of the epitaxial growth of zeolite-β on zeolite SSZ-31; model of the intergrowth (inset, upper); and TEM simulation of this model (inset, lower).

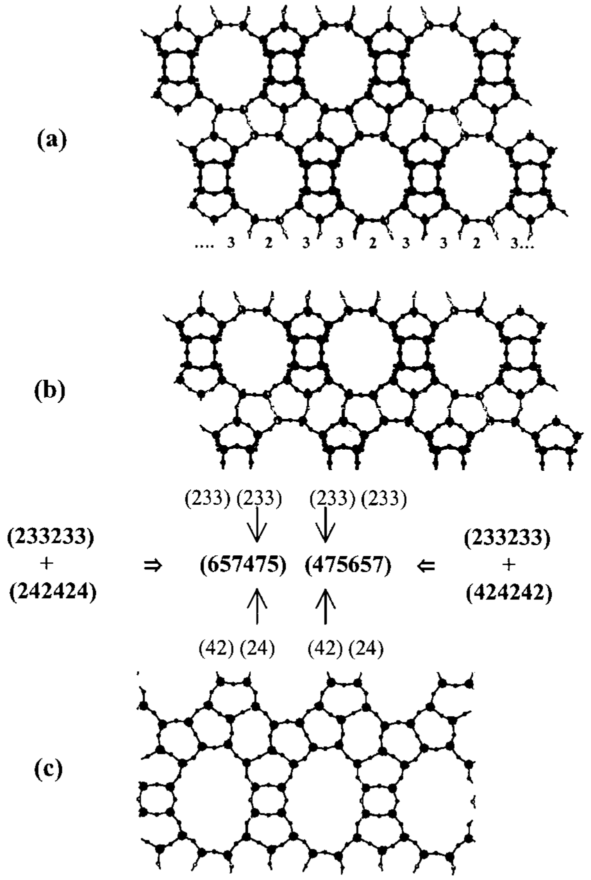

**Fig. 2** (a) Projection of β structure along < 110 > showing the two- and three-membered ring fragments in a (233) sequence; (b) projection along < −110 > showing the half-channels. Each of the eight lowermost silicon atoms is a member of a (233) sequence running alongside a half-channel in the < −110 > direction; (c) projection of SSZ-31 polymorph B along [010] showing the half-channels. Each of the uppermost silicon atoms is a member of a (24) sequence running alongside the half-channel. These sequences are laterally shifted with respect to each other. The generation of the (657475) and (475657) sequences at the interface of zeolite-β with SSZ-31 polymorphs A–D is indicated.

To construct possible interfaces, it is first assumed that the 12-membered composite channels are comprised of six silicate tetrahedra derived from a β channel, and the remaining six tetrahedra from an SSZ-31 channel. We terminate the β structure at a plane parallel to the < −110 > channel direction, leaving six-membered half-channels in this direction and complete channels in the < 110 > direction. Fig. 2(a) shows a view of the β polymorph B along the < 110 > direction, and Fig. 2(b) shows a view along the < −110 > direction showing the half-channels. Since the β channels are enclosed by four-, five- and six-membered rings, the termination results in ring 'fragments' of two or three tetrahedra, which are visible at the bottom of Fig. 2(a). These fragments follow a periodic 2–3–3–2–3–3 . . . sequence (abbreviated to 233), as shown in the figure. At the interface plane, a β half-channel is therefore bounded by two identical 233 sequences (one on either side of the half-channel) propagating down the < −110 > channel direction, as indicated in Fig. 2(b). Similar termination of β polymorph A results in the same structure at the interface. Since β polymorph B is observed at the interface in Fig. 1(b), only this polymorph is considered in the following discussion.

There are eight polymorphs (A–H) of SSZ-31 with different connectivities down the [010] channel direction.[8] The SSZ-31 structure is similarly terminated by a plane parallel to the [010] direction, leaving six-membered half-channels. Fig. 2(c) shows the terminated structure of SSZ-31 polymorph B viewed along the [010] direction, indicating the half-channels. Inspection of this structure in the channel direction shows that the interface plane contains ring fragments of two or four tetrahedra, that form periodic (2–4–2–4–) chains (abbreviated to 24) running along the channel direction. However, these chains are laterally shifted with respect to each other, so that a two-membered fragment on one chain has as its neighbor, a four-membered fragment of the adjacent chain. The two sequences running alongside an SSZ-31 half-channel can be represented as (24) □ (42) for polymorphs A–D. The symbol □ indicates the half-channel as viewed down [010], with one sequence running along its left and right. Polymorphs E–H have adjacent (24) □ (26), and (26) □ (24) half-channels.

The epitaxy is achieved by bonding the half-channels of β and SSZ-31 (*via* oxygen atoms) to form 12-membered interfacial composite channels. The combination of the sequences of zeolite-β with the sequences of SSZ-31 polymorphs A–D results in closed rings following the periodic sequences (475657) ■ (657475); where the symbol ■ indicates the composite channel. Interfaces of β with SSZ-31 polymorphs E–H have two types of composite channels when viewed down the channel direction: (475657) ■ (495858), and (495858) ■ (475657). These channels are adjacent to each other at the interface. The interfaces therefore contain seven-membered rings, and even nine-membered rings in the case of epitaxial growths involving SSZ-31 polymorphs E–H. The two polymorphs of β together with the eight polymorphs of SSZ-31 lead to 16 possible epitaxial growths, with only two possible interfacial structures, (475657) and (495858), as shown above. Considering the unit cell dimensions of the two zeolites, the 2-D rectangular epitaxial unit cell at the interface would have dimensions of 25.2 Å in the SSZ-31 channel direction and 12.33 Å in the perpendicular β channel direction. Composite channels comprising unequal numbers of tetrahedra from each zeolite (*e.g.*, eight from β and four from SSZ-31) do not appear to be feasible due to non-matching bond positions on either side of the interface.

The epitaxy of β polymorph B on SSZ-31 polymorph B is simulated as described above, using the *Cerius*$^2$ Interface Builder. The resulting structure [Fig. 1(b), upper inset] is found to match the TEM image. In the TEM image, the two zeolite-β domains on either side of the SSZ-31 domain appear to be laterally shifted with respect to each other. The structural model proposed above accounts for this observation, since it allows the β structure to be shifted along the channel direction of SSZ-31. This shift is captured in the interface simulation, and appears in the upper inset of Fig. 1(b). A TEM simulation of the interface is also shown (lower inset), and it is seen to match the actual image. However, the information available from the TEM image appears insufficient to identify the SSZ-31 polymorph that is actually involved in the epitaxy. It is also possible that the synthesized sample contains intergrowths of zeolite-β and SSZ-31 in addition to the epitaxial regions that we observe.

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