A Novel Method for the Growth of Silicalite Membranes on Stainless Steel Supports

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Silicalite membranes have been prepared using a novel seeding method. By sonicating silicalite seed crystals in the presence of a stainless steel mesh followed by a controlled hydrothermal synthesis step it has been shown by AFM, SEM, and simple diffusion measurements that coherent membranes are produced. The sonication step anchors the nanometer-sized zeolite seeds to the porous stainless steel support and the subsequent hydrothermal growth produces a zeolite membrane grown on this seed layer.

Introduction

The growth of thin films of zeolites onto solid substrates has been extensively studied as a means of producing selective gas sensors: consequently films of silicalite and other zeolites have been produced on gold,[1,2] silicon,[3,4] and a range of other, electrically conducting supports.[5−7] By replacing the solid support with a porous material, the growth of zeolite films can be used to produce zeolite membranes having potential applications in continuous separation and reaction-separation processes. The growth of zeolite membranes requires some differences in synthetic techniques due to the porous (non-continuous) nature of the supports. A range of zeolite membranes have been successfully grown on the surface of porous stainless steel[8−11] and porous alumina,[12−16] and membranes have also been produced by incorporation of preformed zeolite crystals into a polymeric support such as PDMS.[17−21] Taking into account factors such as cost, mechanical strength, thermal stability, resistance to chemical attack, thermal conductivity, and ease of fabrication, stainless steel is a particularly attractive support material for a microporous membrane. Problems caused by differences in thermal expansion coefficients between support and active layer appear to be much less severe than might have been anticipated.

Silicalite membranes utilize the hydrophobic nature of the all-silica molecular sieve to remove selectively small organic molecules from water streams[22] and are therefore highly desirable as a continuous waste treatment method. While very thin silicalite membranes (<1 μm) have been produced on nonmetallic supports,[12] the thicknesses reported for stainless steel supports have been considerably greater (~50 μm).[9]

In this study we outline a novel method for the growth of coherent silicalite membranes on the surface of a stainless steel (316) mesh. The technique appears to be highly reproducible and can generate films on the order of 1 μm thick. Separation data and component fluxes will be discussed in a forthcoming publication.

Experimental Section

A colloidal silicalite sol was prepared by the method of Persson et al.[23] from a reaction mixture of composition 25:9:

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480:100 SiO_2:TPAOH:H_2O:EtOH, using tetraethyl orthosilicate (TEOS) from BDH (GPR Grade), tetrapropylammonium (TPA) hydroxide and bromide from Fluka (Purum Grade), and sodium hydroxide pellets from BDH (AR Grade). After a synthesis time of 48 h at 100 °C, the resulting product was dialyzed against deionized water to give an aqueous sol of approximately 6% w/w solid content. Particle size was determined by dynamic light scattering using a Malvern Autosizer IIC.

Stainless steel meshes (316S) were a generous gift from Bekaert Fiber Technologies Ltd, Wevelgem, Belgium (ST-3-AL-3, 0.35 mm thick, 975 g/m^2, graded pore diameter 3μm, cut to 3 cm diameter disks). To remove any grease, the meshes were soaked three times for 1 h in toluene and then similarly three times in ethanol. The washed meshes were placed in a glass jar with 50 mL of a 6 wt % aqueous sol of colloidal silicalite. The jar was then placed in an ultrasonic bath and sonicated for 6 h, during which time the temperature rose to ~70 °C. The sonication was carried out using a CAMLAB Transsonic T570/H (HF frequency = 35 kHz) sonic bath.

After sonication, the seeded mesh was dried in a vertical position in air at room temperature overnight. The mesh was then suspended vertically in a PTFE-lined, stainless steel autoclave and a silicalite synthesis mixture added so that the mesh was completely immersed. The synthesis mixture (composition 60:3.0:2.7:6000:240 SiO_2:Na_2O:TPABr:H_2O:EtOH) was prepared as described previously[24] except that the TPABr was added immediately before membrane synthesis and not at the TEOS hydrolysis stage. The autoclave was then placed in an oven at 110 °C and heated statically for 4 days. This composition and temperature were chosen to reduce self-nucleation of the reaction mixture and thus facilitate crystal growth on the nanoscale seeds to form a coherent layer of crystals giving a defect-free film.

The as-synthesized membranes were washed in distilled water and then dried in air at 60 °C overnight. To remove the organic template a calcination step was carried out, the membranes were calcined in flowing air at 540 °C for 6 h. To avoid cracking due to the differing thermal expansion coefficients of the zeolite film and the stainless steel support, ramp rates of 0.25 °C/min were used throughout the calcination procedure. It was found that ramp rates greater than 0.25 °C/min led to cracking of the zeolite film.

The membranes which were produced were tested for major defects and leakage using carbon tetrachloride (CCl_4). The meshes were attached to a glass tube using an epoxy resin, and a reservoir of CCl_4 was placed above the membrane. Below the membrane, a liquid nitrogen trap was maintained at 1 mmHg pressure by a vacuum pump. Since CCl_4 is too large to pass readily through the pores of silicalite, the absence of CCl_4 in the nitrogen trap indicated that a continuous membrane had been synthesized. The membranes were then analyzed using scanning electron microscopy (SEM, Hitatchi S520 microscope) and powder XRD (Philips 1710 diffractometer). To obtain additional information about the process of membrane formation, flat, polished, stainless steel sheets were treated using the sonication/seeding method and then analyzed by atomic force microscopy (AFM) using a Digital Instruments, Nanoscope III instrument.

Results

In our first experiments on membrane synthesis, crystals were grown (90 °C, 7 days) on the seeded mesh support from the same synthesis mixture as that used initially to prepare the silicalite sol. Comparisons of SEM data show that the product (Figure 1) retains the rather open structure of the support (Figure 2) but that a cocoon of intergrown zeolite crystals has been formed around the strands of the mesh (the cross-shaped features are caused by the 90° intergrowth of pairs of silicalite crystals). Not surprisingly, the membrane was readily permeable to CCl_4. By modifying the synthesis conditions, we were able to produce a membrane which is impermeable to CCl_4 (Figure 3). The thickness of a single silicalite crystal layer appears to be approximately 1.5 μm and the cocoons overlap to completely fill the void volume.

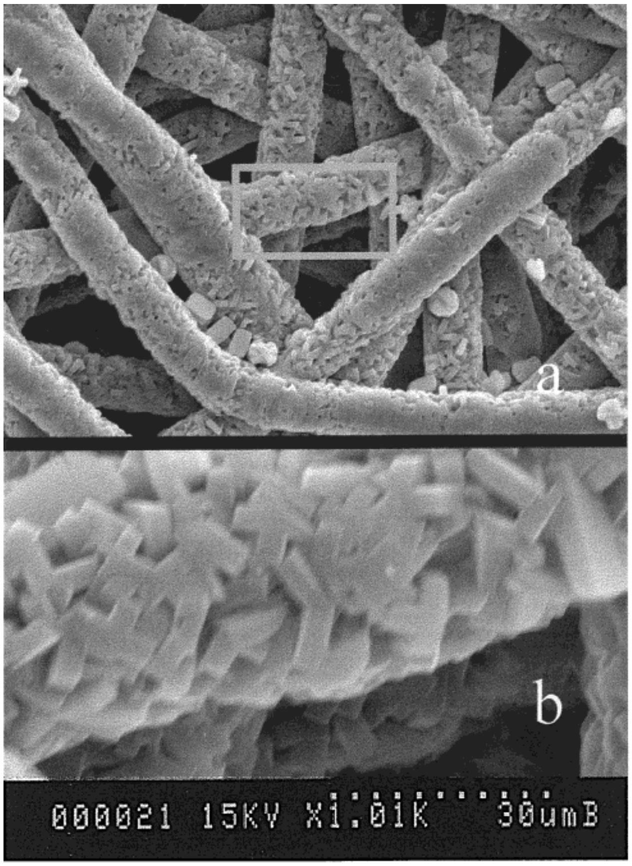

Figure 1. (a) Scanning electron micrograph (SEM) of silicalite growth on a stainless steel mesh and (b) enlargement to show silicalite crystal morphology.

To study the effect of the sonication with the nanocrystal sol, a mesh was mechanically agitated while immersed in a colloidal silicalite suspension ramped to 70 °C. Following the synthesis step (using the modified composition employed for the membrane shown in Figure 3), the mesh was found to be highly permeably to CCl_4, and SEM showed that no crystal growth had occurred on the steel surface. It was considered possible that the sonication itself may be attacking or cleaning the steel surface and therefore promoting growth. However, sonicating in the absence of seeds followed by the synthesis step again gave no zeolite film. In a further investigation of the seeding step, a 316 stainless steel sheet was polished, cleaned, and then cut into three small "coupons." Two of the coupons were treated in the sonicator with a colloidal silicalite suspension while the third was retained as a reference. After sonication, the coupons were air-dried at room temperature overnight. One of the coupons was then washed in a continuous stream of distilled water for 3 h. Using atomic force microscopy, it can be seen (Figure 4a) that the "clean" stainless steel showed the ridges on the surface caused by the polishing but is otherwise featureless. The second coupon shows (Figure 4b) tightly

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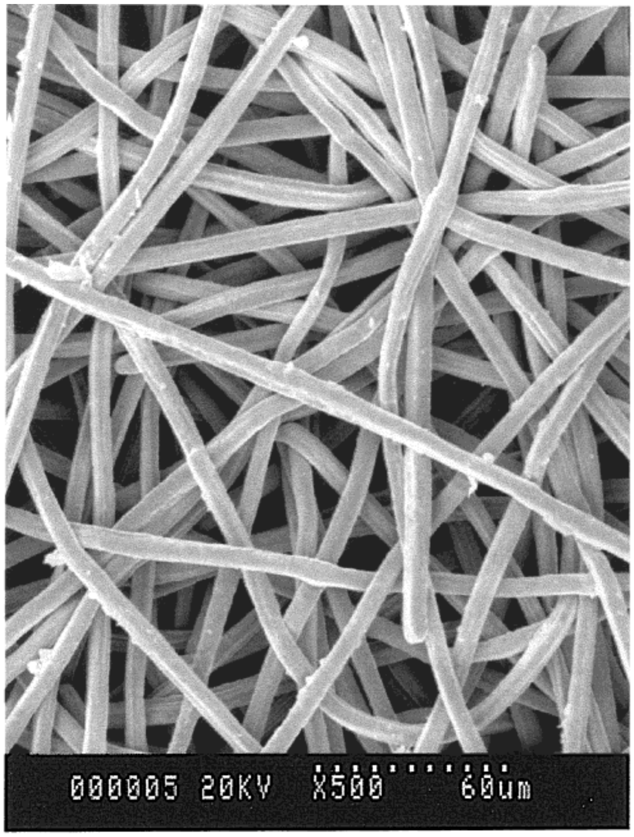

Figure 2. SEM image of an untreated stainless steel mesh.

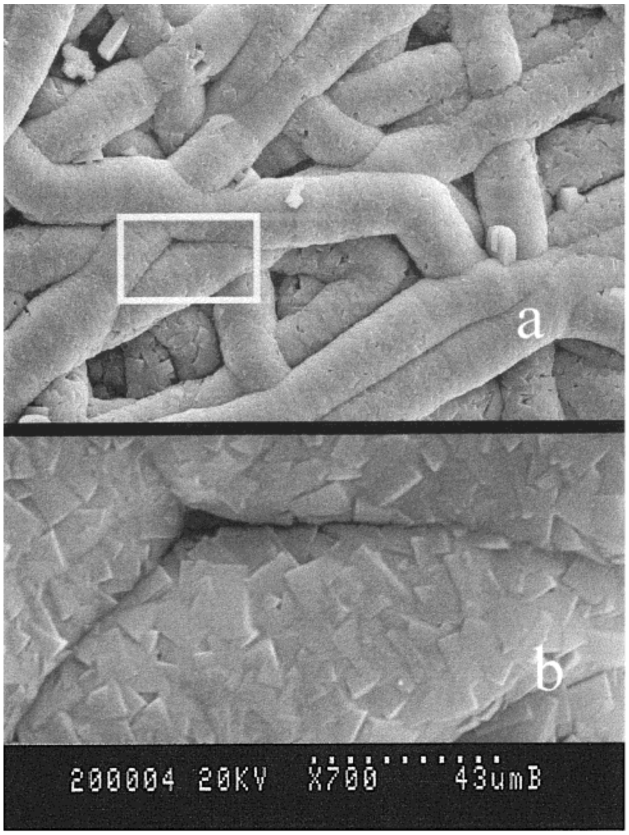

Figure 3. (a) SEM image of a coherent silicalite membrane and (b) enlargement to show silicalite crystal morphology.

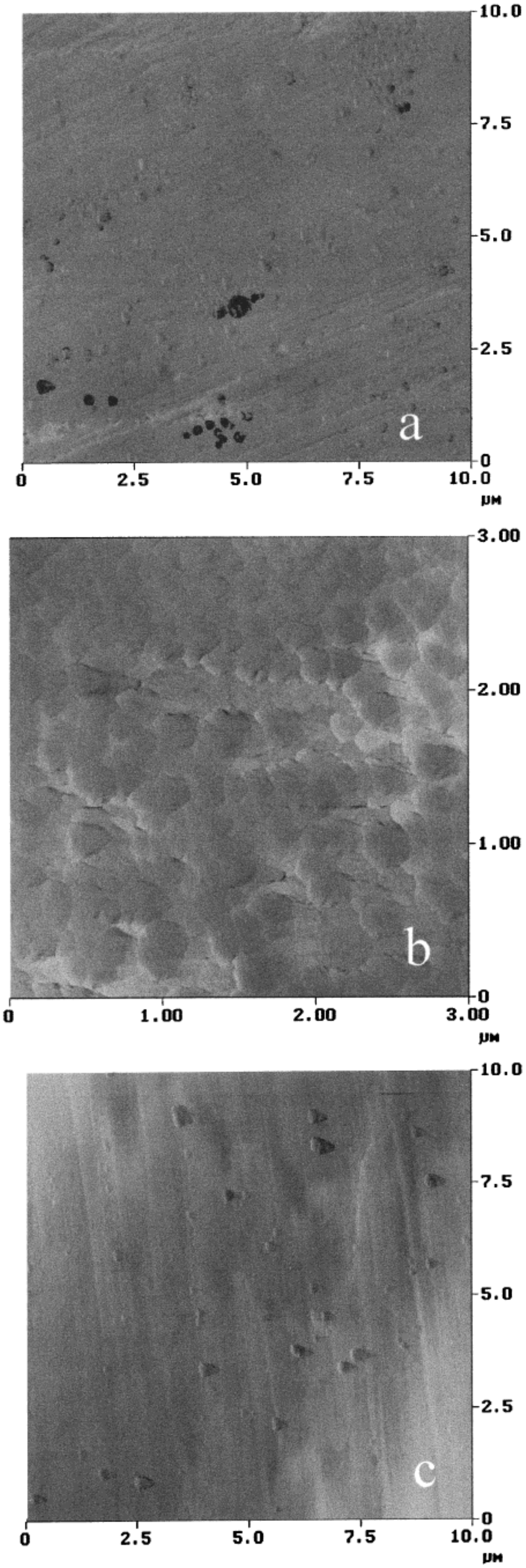

Figure 4. (a) Atomic force micrograph (AFM) of a clean stainless steel coupon, (b) AFM image of a stainless steel coupon, sonicated in silicalite sol, and (c) AFM image of the coupon from panel b after vigorous washing with distilled water.

packed colloidal seeds coating the entire surface of the stainless steel. The AFM shows the colloidal seeds to be on the order of 100 nm in diameter, which agrees with the value measured for the sol by dynamic light scattering. Vigorous washing of the coupon in distilled water completely removed the colloidal film (Figure 4c), returning the steel to the appearance of the untreated material. Repeating this entire experiment using mechanical agitation rather than sonication surprisingly showed that a good coverage of the stainless steel by nanocrystals was achieved. However, the film of colloidal crystals was readily removed by immersing the coupon in distilled water for 10 min. Since immersion of the sonicated coupon in distilled water for 10 min had no effect on the AFM image, it would appear that the sonication step has the effect of "binding" the seeds to the surface, whereas the mechanical agitation deposits a thin layer which is easily removed.

Discussion

Sonication of a stainless steel mesh in the presence of a colloidal silicalite sol apparently has the effect of entirely coating the surface of the metal with a thin film of the nanocrystalline molecular sieve precursor. This colloidal film acts as a seed layer upon which a cocoon of more macrocrystalline silicalite may be grown. If the growth is allowed to proceed so that the voids between the strands of the mesh are filled, a coherent membrane that is impermeable to CCl_4 is produced. The adhesion of the seed layer through the sonication procedure does not seem to affect the surface of the metal. It was initially suspected that a pitting effect (caused by localized high pH at the surface of a nanocrystal, coupled with the sonication) may be etching the surface of the metal and thereby facilitating the growth of the film. However, AFM results show the surface of the metal to be unaffected after the seed layer is removed. The seed crystals themselves also appear unaffected by the sonication, since the size of the particles in the AFM study are consistent with those of the as-synthesized seeds in the silicalite sol. However, the colloidal seed layer is quite firmly fixed to the surface of the metal, since while it can be washed off using a vigorous and prolonged treatment with distilled water, it is not dislodged by simple immersion in water. The formation of an incomplete membrane in the absence of sonication may be explained by the facile removal of any colloidal seed layer from the surface of the mesh on immersion in the synthesis mixture for the growth step. The sonicated seed layer is more robust and persists to form a zeolite film on the surface of the steel during the hydrothermal growth step.

A comparison of the above zeolite films with those produced by Sterte and co-workers[12,25] shows a similar affect of colloidal seeding. However, in the case of the solid gold, silicon, and quartz supports which have been used, a charge reversing polymer is used to prepare the surface of the support prior to treatment with the colloidal sol. An alternative procedure has been demonstrated by Tsapatsis et al.[26] involving colloidal seeds on ceramic supports using a dip-coating technique. This method is reported to produce 25−40 μm thick, oriented MFI membranes on α-Al_2O_3 supports. In the case of the sonicated seeding, a similar effect appears to be produced without pretreatment and the technique appears very suitable for use on porous stainless steel supports.

In Figure 1, there would appear to be a large number of intergrown crystals with the *c*-axis normal to the surface of the stainless steel: this is shown by the large number of characteristic "crosses" which are visible. In Figure 3, it is apparent that more a coherent zeolite film has been formed, and it appears that the crystals have grown "along" the wires of the mesh, with predominantly the (010) faces of the crystals growing out from the wire. In the synthesis of the coherent zeolite membrane (Figure 3), the composition of the reaction mixture differed considerably from that used for the formation of the film shown in Figure 1, the former being more dilute, with a lower base/SiO_2 ratio and appreciable sodium content. This is consistent with the work of Jansen et al.,[27] who have studied the growth of MFI-type molecular sieves on a variety of supports and observed lateral or axial crystal orientation, depending on synthesis composition and reaction conditions.

Conclusions

Sonication of a stainless steel support in the presence of a colloidal silicalite sol, followed by drying at room temperature, has the effect of coating the surface of the stainless steel with a moderately tenacious seed crystal layer. By means of a subsequent controlled hydrothermal growth step, a zeolite membrane can be produced which has been shown to be essentially pinhole free. This process may be extended to other zeolite systems (e.g. ZSM-5,TS-1 and Zeolite A), and production of these membranes will be discussed in a forthcoming publication.

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