

Oriented Molecular Sieve Films by Heteroepitaxial Growth

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ABSTRACT

In this report, we demonstrate the use of epitaxial growth of one molecular sieve (ETS-10) on another (ETS-4) to fabricate preferentially oriented molecular sieve films. Highly *b*-oriented but poorly intergrown ETS-4 precursor layer is first prepared. Then by the secondary growth method, highly *a*-/*b*-oriented ETS-10 molecular sieve film is fabricated under a hydrothermal condition that leads to heteroepitaxial growth of ETS-10 on ETS-4. X-ray diffraction and scanning electron microscopy (SEM) are utilized to determine the preferred orientation.

Keywords: microporous molecular sieves, zeolites, inorganic films, preferred orientation.

INTRODUCTION

Microporous molecular sieves are crystalline inorganic materials with their pore dimensions in the range of molecular size (see Figure 1). Their pore structures are well-defined with a variety of choices in size ranging from sub-nanometer to nanometer and in dimensionality from being one dimensional to being three dimensional. Molecular sieves find applications in catalysis, ion exchange and adsorption mostly in the form of powder. Recently, fabrication of microporous molecular sieve films with potential uses as selective membranes, membrane reactors, chemical sensors, optical devices as well as in other new applications attracts research interest [1-13]. Owing to the dramatic expansion of the microporous inorganic materials during the last decade, Cheetham et al. envisioned the possibility of microporous molecular sieve materials having remarkable electronic properties: for example, ferromagnetism, metal- semiconductor transition, giant magnetoresistance, ferro-electricity, combined ionic/electric conductivity, or even superconductivity [14]. Most of the applications in the area of nanotechnology are based on the molecular films. The crystallinity of these materials along with being a main advantage imposes demanding challenges for film fabrication [4]. It is well recognized that these challenges include the control of preferred orientation that is important for two main reasons. First, for framework structures other than cubic, preferred orientation can be reflected in the transport and other (e.g.,

optical, electronic) properties of the film [5]. Second, different orientations can result in differences of the grain boundary structure which in turn influences the overall performance of a film, especially in membrane applications [15]. Other, system specific effects have been reported, as for example, the influence of preferred orientation on the film's surface roughness that can affect, among other properties, the optical transparency of a molecular sieve coating [11]. Many studies have attempted to provide

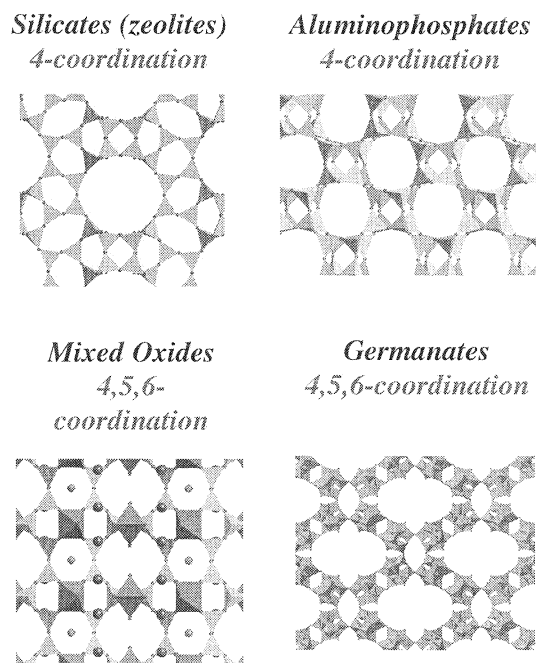


Figure 1: Microporous molecular sieves materials (ref. [1])

methods for achieving preferred orientation in molecular sieve films. Jansen et al. first discovered *in situ* preparation conditions that can give rise to b-out-of-plane oriented and intergrown MFI layers on silica wafers [15] and this approach was recently extended by Yan and coworkers [8]. However, because of insufficient understanding of nucleation and growth processes in hydrothermal systems, especially with respect to controlling nucleation density on arbitrary supports and particle shape evolution, the success of *in situ* methods in yielding oriented films is limited to few zeolites and desirable orientations. Alternative

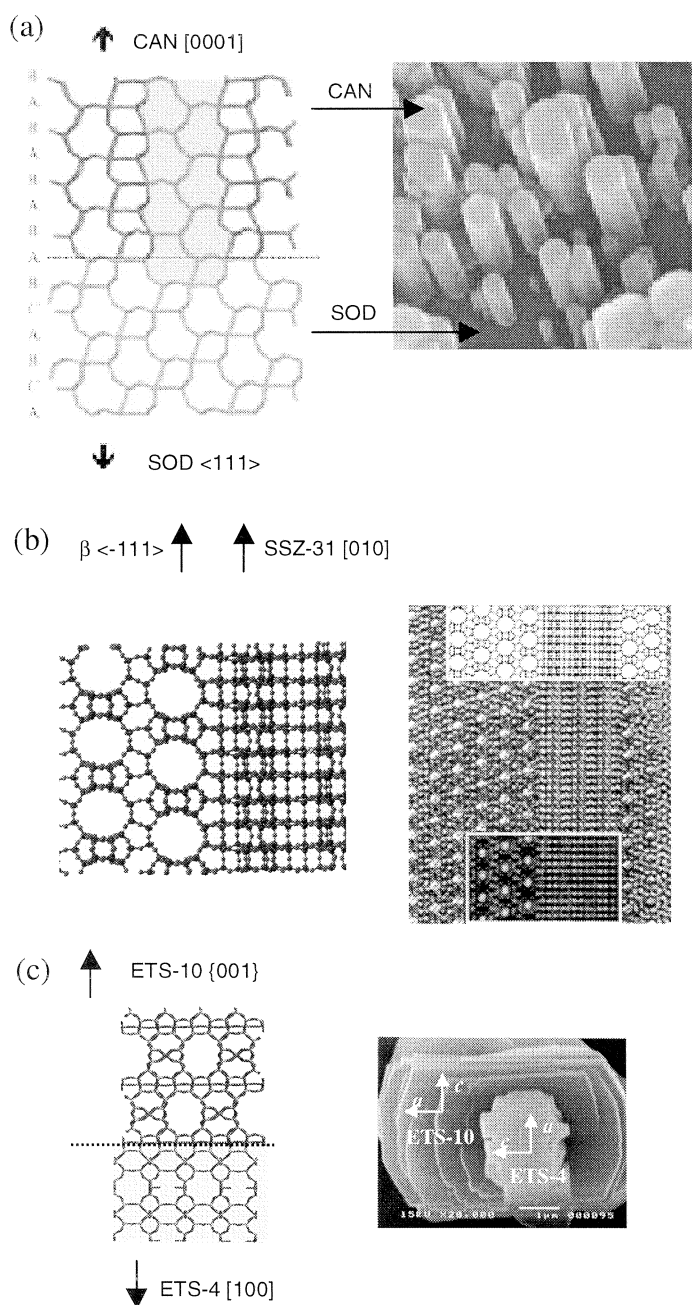


Figure 2: Examples of epitaxial growth: (a) Cancrinite on sodalite (ref. [21]), (b) Zeolite β on SSZ-31 (ref. [22]), (c) ETS-10 on ETS-4 (ref. [23])

approaches to *in situ* growth that attempt to decouple nucleation from growth, rely on pre-seeding the support of the molecular sieve film with a seed layer made up from particles or fragments of the same material [9-13,16-20]. Seed layers can be preferentially or randomly oriented. In the case of preferentially oriented layers, epitaxial growth can lead to oriented films [9,10,17], while in the case of

randomly oriented layers preferential orientation can gradually develop as the film thickens based on the well known principle of evolutionary selection (Van der Drifts growth) [11]. Secondary growth of seed layers has been reported to result in preferentially oriented films. However, the success is still limited by available shapes/sizes and deposition methods of seed particles and by constraints in adjusting the growth velocities of crystal planes in a given molecular sieve.

In an effort to extend the secondary growth method to other molecular sieve types and orientations, we demonstrate here that heteroepitaxial growth of one molecular sieve on another can be a promising way to the formation of a preferentially oriented film of a molecular sieve. Heteroepitaxial growth of ETS-10 on ETS-4 is given as an example.

Certain molecular sieves which are composed of the same or similar building blocks with the different stacking orders have been reported to show epitaxial growth. Some examples of molecular sieves showing such epitaxial growth are given in Figure 2. Epitaxial growth of cancrinite(CAN) on certain faces of sodalite (SOD) single crystals prepared by mechanical polishing was reported by Okubo et al [21] shown in Figure 2(a). Nair et al [22] reported the epitaxial growth of zeolite β on SSZ-31 nanofibers shown in Figure 2(b). We have recently reported a condition where ETS-10 crystals are grown epitaxially on (100) faces of ETS-4 [23] shown in Figure 2(c).

ETS-10 is a microporous zeolite-like material consisting of $[\text{TiO}_6]$ octahedra and $[\text{SiO}_4]$ tetrahedra [24] while a structurally related material, ETS-4, has distinctive $[\text{TiO}_5]$ pyramidal-squares as well as octahedral titania and tetrahedral silica [25,26]. In ETS-10, there are twelve membered rings (12MR) in all three directions, with straight channels in the *a*- and *b*-directions and nonlinear channels along the *c*-direction. In ETS-4, 12 MRs are blocked by the pronounced stacking disorder along the *c*-direction and as a result transport is controlled by a 2-D channel system with limiting 8MR openings. ETS materials have potential applications in catalysis, adsorption and ion exchange as well as in membrane separations [27,28]. In addition, they have interesting optical properties due to the monoatomic quantum wire character of the corner sharing titania chains [29].

EXPERIMENTAL

To use this heteroepitaxial growth in the formation of oriented membranes, highly *b*-oriented but poorly intergrown ETS-4 precursor layer was first prepared on asymmetric porous titania substrate using the secondary growth technique described elsewhere [27]. The non-intergrown needle-like ETS-4 precursor layer was then subjected to secondary growth at 200°C for various times using a mixture with molar composition of 5.71 SiO_2 : 1 TiO_2 : 1.9KF : 7.2NaOH : 168.25 H_2O , which led to the heteroepitaxial growth of ETS-10. For the synthesis,

sodium silicate solution (Aldrich, 27% SiO₂, 14% NaOH) and titanium (III) chloride solution (Fisher Scientific, 10%, stabilized with HCl) were used as a Si and a Ti source, respectively. In a typical experiment, sodium hydroxide (4.33g) was dissolved in 34.4g deionized water (solution I). 50g Sodium silicate solution was diluted with 34.4g deionized water (solution II). Then solution I and II were thoroughly mixed. Finally, 30.34g titanium (III) chloride was added very slowly under vigorous stirring. The final mixture was stirred for additional 30 min. to achieve homogeneous solution. The resulting thick purple solution was then introduced into a stainless steel autoclave (Parr) along with ETS-4 precursor film and crystallized at 200°C with varying crystallization times. After the autoclave was cooled to room temperature, the film was washed thoroughly with de-ionized water and dried at room temperature overnight. Powder X-ray diffraction patterns were collected on a Philips X'Pert diffractometer.

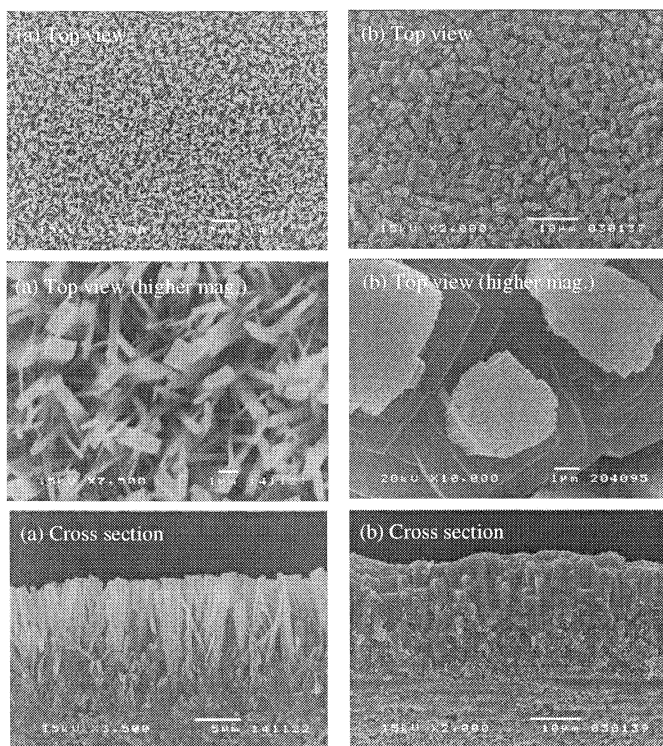


Figure 3: SEM images of the ETS-4 precursor layer (a), and of the ETS-10/4 film synthesized by heteroepitaxial growth on the ETS-4 precursor layers after 20 hrs (b).

RESULTS AND DISCUSSION

Figure 3 shows initial and final images of the ETS-10/4 film. The time-evolution of the film (not shown here) clearly indicates that ETS-10 starts growing on the ETS-4 crystals of the precursor layer, eventually filling the gaps between the ETS-4 crystals. That leads to a well-intergrown ETS-10/4 membrane. From the epitaxial relationship

shown in Figure 2(c) and the preferred orientation of the ETS-4 layer, it is expected that the ETS-10 crystals will be *a*- (or, equivalently, *b*-) out-of-plane oriented. This is corroborated by the SEM top view images of the film (compare Figures 3(b) and 2(c)) and by analysis of X-ray diffraction (XRD) results. In previous reports, analysis of the preferred orientation of molecular sieve films has been performed by pole figure analysis [11,12] grazing incidence X-ray diffraction [30] and at the qualitative level by use of XRD data collected in a Bragg-Brentano geometry [10,31]. For the purpose of this report, we used the latter method to determine preferred orientation of the films.

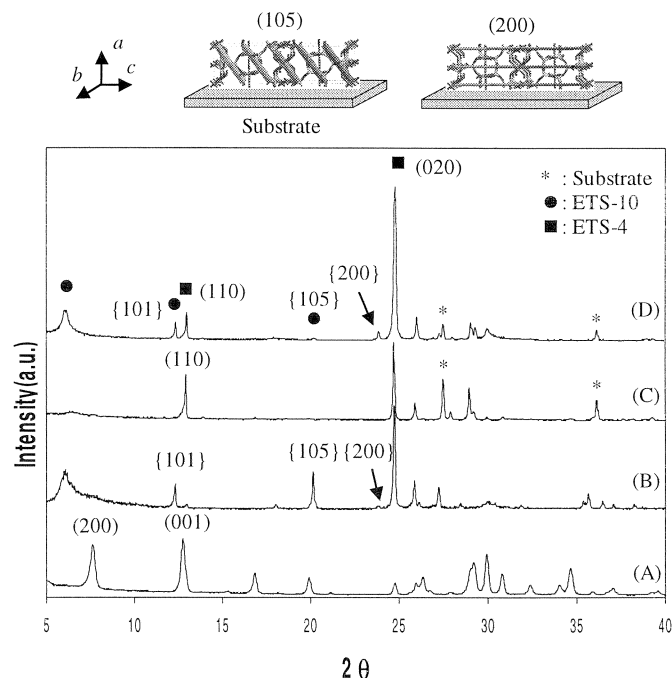


Figure 4: X-ray diffraction patterns: (A) ETS-4 powder, (B) ETS-10 powder, (C) ETS-4 precursor layer, and (D) ETS-10/4 film grown for 20 hrs. Indexing of ETS-10 is based on the superposition model by Wang et al [32]. The schemes show the orientation of the (105) and (200) planes with respect to the substrate for *a*-out-of-plane oriented ETS-10.

Figure 4 shows XRD patterns collected for ETS-4 (trace A) and ETS-10 (B) powders and from the ETS-4 precursor layer (C) of Figure 3(a), and the final ETS-10/4 film (D) of Figure 3(b). A comparison of trace A and C of Figure 4 confirms the *b*-out-of-plane orientation of the ETS-4 precursor layer [27]. Trace D, along with the reflections corresponding to the oriented ETS-4 film, clearly shows the appearance of ETS-10 peaks however, with drastic changes in the relative intensities compared to the powder pattern of trace (B). An unambiguous evidence of *a*- (or *b*-) out-of-plane preferred orientation is provided by comparison of the {105} and {200} reflections. The crystallographic preferred orientation, CPO, for these reflections is larger

than 50, indicating strong orientation. The CPO was calculated using the following formula [31],

$$\text{CPO}_{\frac{200}{105}} = \left[\frac{I_{200}}{I_{105}} \right]_D - \left[\frac{I_{200}}{I_{105}} \right]_B \bigg/ \left[\frac{I_{200}}{I_{105}} \right]_B$$

where I is the integrated intensity of the corresponding reflection at the indicated trace.

The diffraction pattern of ETS-10 powders, confirm the preferred orientation. It is clearly shown that the intensities of the (101) or (011) and the (020) or (200) peaks of ETS-10 gradually increase over time (not shown here), and their relative intensities by far exceed those observed in the powder XRD pattern of ETS-10.

CONCLUSION

We demonstrated that heteroepitaxial growth of one molecular sieve (ETS-10) on another (ETS-4) could be an alternative way to fabricate highly oriented molecular sieve films. X-ray diffraction patterns along with SEM images indicated the preferred orientation of the ETS-10 film with the *a*-/*b*-direction perpendicular to the substrate. The extension of the secondary growth procedure to include heteroepitaxial growth as described here should be applicable in other microporous molecular sieves. For example, based on the method presented here, *b*-/*or a*- out-of-plane-oriented zeolite beta films could be grown on *c*-out-of-plane oriented films of SSZ-31. More interestingly, the orientation of molecular sieve membranes fabricated by heteroepitaxial growth can be adjusted by changing the orientation of the precursor layers. For example, a *c*-oriented ETS-10 membrane, could be fabricated on *a*-oriented ETS-4 precursor layer.

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REFERENCES

- [1] M. Tsapatsis, *AIChE J.*, 48, 654, 2002
- [2] T. T. Bein, *Chem. Mater.*, 8, 1636, 1996
- [3] M. E. Davis, *Nature*, 417, 813, 2002
- [4] M. Tsapatsis, G. Xomeritakis, H. Hillhouse, S. Nair, V. Nikolakis, G. Bonilla, Z. Lai. *Cattech*, 3, 148, 2001
- [5] J. Caro, M. Noack, P. Kolsch, R. Schafer, *Micropor. Mesopor. Mat.*, 38, 3, 2000
- [6] G. A. Ozin, A. Kuperman, A. Stein, *Angew. Chem. Int. Ed.*, 28, 359, 1989
- [7] H. H. Funke, M. G. Kovalchick, J. L. Falconer, D. Noble, *Ind. Eng. Chem. Res.*, 35, 1575, 1996
- [8] Z. B. Wang, Y. S. Yan, *Chem. Mater.*, 13, 1101, 2001
- [9] S. Y. Choi, Y. J. Lee, Y. S. Park, K. Ha, K. B. Yoon, *J. Am. Chem. Soc.*, 122, 5201, 2000
- [10] L. C. Boudreau, M. Tsapatsis, *Chem. Mater.*, 9, 1705, 1997
- [11] A. Gouzinis, M. Tsapatsis, *Chem. Mater.*, 10, 2497, 1998
- [12] M. C. Lovallo, M. Tsapatsis, *AIChE J.*, 42, 3020, 1996
- [13] G. Xomeritakis, Z. Lai, M. Tsapatsis, *Ind. Eng. Chem. Res.*, 40, 544, 2001
- [14] A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem. Int. Ed.*, 38, 3268, 1999
- [15] J. C. Jansen, G. M. Rosmalen, *J. Cryst. Growth*, 128, 1150, 1993
- [16] K. J. Balkus, T. Munoz, M. E. Gimon-Kinsel, *Chem. Mater.*, 10, 464-466, 1998
- [17] S. Mintova, J. Hedlund, B. Schoeman, V. Valtchev, J. Sterte, *Chem. Comm.*, 1, 15, 1997
- [18] J. Hedlund, J. Sterte, M. Anthonis, A. J. Bons, A. J., B. Carstensen, N. Corcoran, D. Cox, H. Deckman, W. De Gijst, P. P. de Moor, F. Lai, J. McHenry, W. Mortier, J. Reinso, *Micro. Meso. Mater.*, 52, 179, 2002
- [19] M. Kondo, M. Komori, H. Kita, K. Okamoto, *J. Membr. Sci.*, 133, 133, 1997
- [20] T. Okubo, T. Wakihara, J. Plevert, S. Nair, M. Tsapatsis, Y. Ogawa, H. Komiyama, M. Yoshimura, M. E. Davis, *Angew. Chem. Int. Ed.*, 40, 1069, 2001
- [21] S. Nair, L. A. Villaescusa, M. A. Camblor, M. Tsapatsis, *Chem. Commun.*, 911, 1999
- [22] H.-K. Jeong, J. Krohn, K. Sujaoti, M. Tsapatsis, *J. Am. Chem. Soc.*, 124, 12966, 2002
- [23] M. W. Anderson, O. Terasaki, T. Ohsuna, T., P. J. O. Malley, A. Philippou, S. P. MacKay, A. Ferreira, J. Rocha, S. Lidin, *Philos. Mag. B*, 71, 813, 1995
- [24] S. Nair, H.-K. Jeong, A. Chandrasekaran, C. M. Braunbarth, M. Tsapatsis, S. M. Kuznicki, *Chem. Mater.*, 13, 4247, 2001
- [25] C. M. Braunbarth, H. W. Hillhouse, S. Nair, M. Tsapatsis, A. Burton, R. F. Lobo, R. M. Jabubinas, S. M. Kuznicki, *Chem. Mater.*, 12, 1857, 2000
- [26] C. M. Braunbarth, L. Boudreau, M. Tsapatsis, *J. Membr. Sci.*, 174, 31, 2000
- [27] S. M. Kuznicki, V. A. Bell, S. Nair, H. W. Hillhouse, R. M. Jacobina, C. M. Braunbarth, B. H. Toby, M. Tsapatsis, *Nature*, 412, 720, 2001
- [28] E. Borello, C. Lamberti, S. Bordiga, A. Zecchina, C. O. Arean, *Appl. Phys. Lett.*, 71, 2319, 1997
- [29] T. H. Metzger, S. Mintova, T. Bein, *Micropor. Mesopor. Mater.*, 43, 191, 2001
- [30] J. P. Verduijn, A.-J. Bons, M. H. c. Anthonis, L. R. Czarnetzki, *WO 96/01683*, 1996
- [31] X. Wang, A. J. Jacobson, *Chem. Commun.* 973, 1999