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Growth mechanism of a preferentially oriented mordenite membrane

LI Gang (厉 刚)[†1], LIN Rui-sen (林瑞森)[1], KIKUCHI Eiichi[2], MATSUKATA Masahiko[2]

(*[1]Department of Chemistry, Zhejiang University, Hangzhou 310027, China*)
(*[2]Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*)
[†]E-mail: gli@zju.edu.cn

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Abstract: A preferentially oriented mordenite membrane was successfully prepared on a seeded porous α-alumina support. Characterization results of XRD (X-ray diffractometer) and FE-SEM (field emission scanning electron microscope) revealed that evolutionary selection might predominantly contribute to the formation of the sharply oriented mordenite membrane. The necessary conditions under which evolutionary selection occurs are: (a) the number density of nuclei on the support surface should be high enough at the early stage; (b) the crystals should grow fastest along one direction; and (c) the zeolite layer should proceed via the successive growth of the crystals nucleated on the support surface instead of the accumulation of the crystals formed in the bulk solution.

Key words: Mordenite, Zeolite membrane, Orientation, Evolutionary selection
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INTRODUCTION

Zeolite membranes have been investigated for many years due to their promising applications in separations (Tavolaro and Drioli, 1999) and membrane reactors (Coronas and Santamaria, 1999). One of the challenges in the preparation of zeolite membranes is the control of the crystal orientation, especially for zeolites that have an anisotropic pore structure (Caro *et al.*, 2000). An ideal case is that the channels in the zeolite crystals are perpendicular to the support surface, resulting in a maximum permeation flux. For most of the zeolite membranes reported so far, however, the crystals are always randomly or partially oriented. Only a few zeolite types such as MFI, LTA, MWW and DON have been prepared into oriented films or membranes (Lovallo and Tsapatsis, 1996; Boudreau *et al.*, 1999; Munoz and Balkus, 1999; Cheng *et al.*, 2001).

Owing to its controllable pore size by ion exchange, strong hydrophilicity, resistance in acidic media and catalytic properties, mordenite (MOR) zeolite has also been studied as an attractive membrane material for separations (Suzuki *et al.*, 1990; Nishiyama *et al.*, 1995; Tavolaro *et al.*, 2000; Lin *et al.*, 2000; Zhang *et al.*, 2002). The crystals in most of these membranes, however, are always randomly oriented. On the other hand, mordenite zeolite contains one-dimensional channels parallel to the crystallographic *c*-axis with a pore opening of 0.65 nm×0.70 nm. It suggests that the crystals in the mordenite membrane should be oriented with their *c*-axes perpendicular to the support surface in order to reduce the transport resistance through the membrane. In this paper, we report the preparation of such a preferentially oriented mordenite membrane and its growth mechanism. The pervaporation properties of these oriented mordenite membranes have been reported elsewhere (Li *et al.*, 2003).

EXPERIMENTAL DETAILS

Asymmetric porous α-Al_2O_3 plates (NGK Insulators Co., Japan) with an average pore diameter of 100 nm in the top layer were used as supports. The supports were cleaned successively in acetone and deionized water for 20 min under ultrasonication before use.

In most cases, the support surface was coated with seeds by use of the dip-coating method prior to hydrothermal treatment. The colloidal mordenite suspension (solid content=3×10^{-3} g/cm^3, pH=6.0) for dip-coating was prepared as follows. Commercially available mordenite powder (HSZ 600HOA, SiO_2/Al_2O_3=10.2, Tosoh Co., Japan) was first crushed in an agate mortar. The crushed powder was then mixed with an appropriate amount of water in a beaker to form slurry. The slurry was treated in an ultrasonic bath and then kept at room temperature for several days. Due to the gravitational effect, larger particles settled down to the bottom of the beaker, leaving a stable milky suspension at the upper part of the slurry. This milky suspension was used for dip-coating.

The dip-coating process was carried out as follows. The support was first dipped in the colloidal suspension for 2 min, then withdrawn vertically at a slow rate, and finally dried for 30 min at 293 K and subsequently for 30 min at 393 K. This process was implemented twice.

A gel with molar composition of 10 Na_2O:0.15 Al_2O_3:36 SiO_2:440 H_2O was prepared at room temperature by dissolving sodium hydroxide (97.0 wt%, Kanto Chemical Co., Inc., Japan), sodium aluminate (34.0–39.0 wt% Al_2O_3, Kanto Chemical Co., Inc., Japan) and silica sol (30–31 wt% SiO_2, Nissan Chemical Industries Ltd., Japan) in water under stirring. A clear solution was obtained after stirring at 323 K for 3–4 h. The seeded or unseeded support was held vertically in this solution and sealed in a Teflon-lined autoclave. Hydrothermal crystallization was carried out at 453 K for various periods of time. After the crystallization, the support was recovered, thoroughly washed with deionized water, and then dried at 393 K.

The morphology of the membrane was characterized using a field emission scanning electron microscope (FE-SEM, Hitachi, S4500S) and a scanning electron microscope (SEM, Hitachi, S2150). The phase and the orientation of the crystals formed on the support surface were characterized using an X-ray diffractometer (XRD) with a Cu K_α radiation source (Rigaku RINT 2100).

RESULTS AND DISCUSSION

Fig.1 shows the XRD pattern of an oriented mordenite membrane grown on a seeded porous α-alumina plate after crystallization at 453 K for 48 h, together with that of mordenite powder for comparison. Compared with the XRD pattern of powder sample, the intensity of the (002) reflection of the crystals in the membrane was fairly stronger while the other peaks were weaker. Such a feature indicates that surface crystals in the membrane are predominantly oriented with their *c*-axes perpendicular to the support surface. SEM images of this oriented membrane are shown in Fig.2. Highly oriented crystals can be clearly observed in the membrane surface, which agrees with the XRD data.

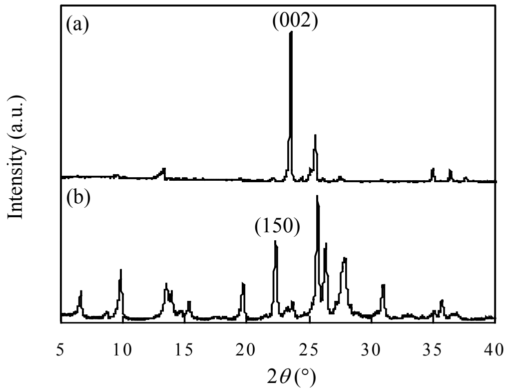
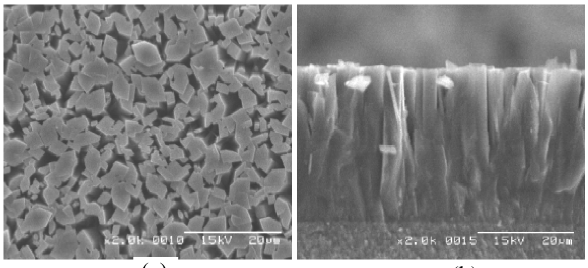


Fig.1 XRD patterns: (a) a mordenite membrane prepared at 453 K for 48 h on a seeded porous α-alumina plate; (b) mordenite powder



(a) (b)

Fig.2 SEM images of a mordenite membrane prepared at 453 K for 48 h on a seeded porous α-alumina plate: (a) top view; (b) cross sectional view

To elucidate the growth process of oriented mordenite crystals on the porous support, the evolution in the degree of orientation of mordenite crystals with crystallization time was followed by means of XRD and FE-SEM methods. The degree of orientation of mordenite crystals in the membrane is defined here as the ratio (k) of the intensity of the (002) reflection to that of the (150) reflection. According to this definition, the larger the k value, the more oriented the crystals in the membrane. As shown in Fig.3, the *k* values increase with crystallization time, indicating that the crystals in the membrane surface become more and more oriented with their (002) faces parallel to the support surface as the crystallization time increases. For comparison, the *k* value is only about 0.21 for mordenite powder.

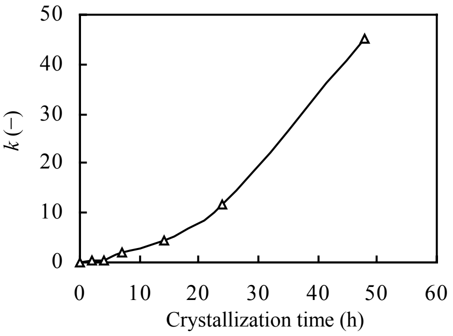
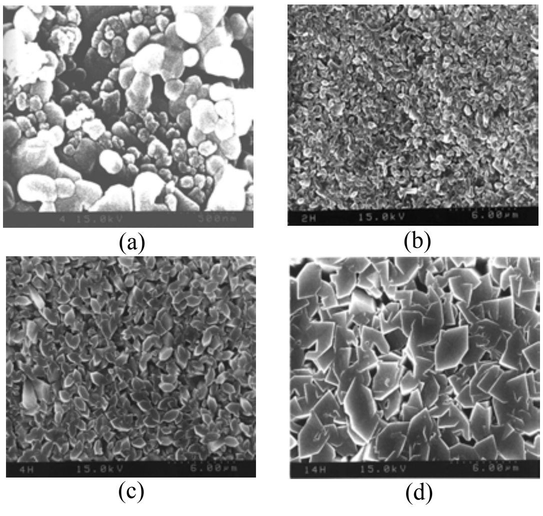


Fig.3 The *k* value as a function of crystallization time

Fig.4 shows typical FE-SEM top views of the seeded support and several membranes obtained after different periods of time. It can be seen that the support surface is not completely covered with seeds. After 2 h, the support surface was covered with a great number of small well-developed crystals with random orientations. As the crystallization time increased, the size of the crystals became larger and the preferred orientation appeared. In addition, the number of the crystals per unit area also decreased with crystallization time and the membrane surface was progressively covered with oriented crystals.



(a) (b)

(c) (d)

Fig.4 FE-SEM top views (a) seeded α-alumina support and membranes after hydrothermal treatment at 453 K for various periods of time: (b) 2 h; (c) 4 h; (d) 14 h

The FE-SEM cross sectional views of these membranes show that the thickness of the zeolite layer increases almost linearly with crystallization time at a rate of ca. 0.6 μm/h, as shown in Fig.5. It suggests that mordenite crystals grow faster along the *c*-axis (ca. 0.6 μm/h) than along *a*- or *b*-axis (ca. 0.3 μm/h, estimated from Fig.4). Fig.5 also shows another important feature: there is hardly induction time. Thus, it can be concluded that the growth of the zeolite layer proceeds predominantly via the direct growth of the seeds instead of the accumulation of the crystals formed in the bulk solution.

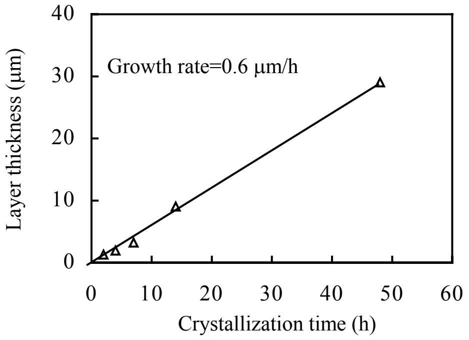


Fig.5 Dependence of the layer thickness on crystallization time

On the other hand, it should be noted that mordenite crystals grown on an unseeded support had random orientation. In contrast to the case of the seeded support, much fewer crystals were observed on the unseeded support at the early crystallization stage. It indicates that the formation of oriented crystals strongly depends on the number density of the crystals on the support at the early stage. The use of seeding apparently increases the nucleation sites on the support surface.

From the above observations, we infer that the preferentially oriented mordenite membrane was formed according to the “evolutionary selection” mechanism, first proposed by van der Drift (1967) to explain the preferred orientation of a vapor-deposited PbO layer. A simple scheme of this mechanism is shown in Fig.6.

A great number of the crystals with random orientations are first formed on the seeded support in the very early stage. These crystals can grow in all possible directions. Upon growth, the crystals touch each other. When two crystals meet, the growth front of a less steep crystal touches the flank of a steeper one

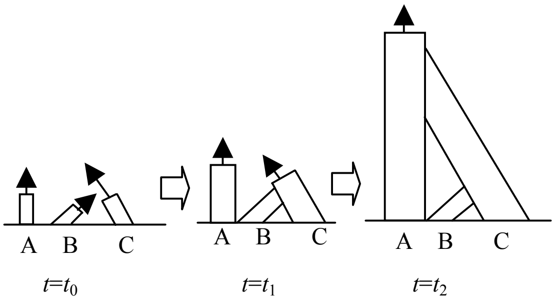


Fig.6 Schematic representation of the evolutionary selection processes

t=t_0: Crystals A, B and C have different orientation;

t=t_1: Crystal B grows to meet crystal C and its growth is stopped. After this selection, crystals A and C are survived and continue to grow;

t=t_2: Crystal C grows to meet crystal A and its growth is stopped. After this selection, only crystal A is survived, because its vertical growth rate is faster than that of the other two

and thereafter stops growing, whereas the steeper one continues to grow. Similarly, when this steeper crystal meets a much steeper crystal, it ends in the flank of the much steeper one and the latter can grow further. As a consequence of such "evolutionary selection" processes, many crystals are embedded under the growing layer, while only those crystals with their fastest growth direction vertical to the support surface survive.

As discussed above, mordenite crystals grow fastest along the crystallographic c-axis. Therefore, only the crystals with their c-axes perpendicular to the support can survive while those with their c-axes inclining from the normal of the support are embedded under the top layer. A pronounced feature of such a growth mode is that the degree of orientation of crystals increases with crystallization time. This is in complete agreement with FE-SEM and XRD observations.

For the case of an unseeded support, the role of the "evolutionary selection" process becomes less effective due to the low number density of the crystals on the support. As a result, crystals grown on an unseeded support surface are randomly oriented.

CONCLUSION

XRD and FE-SEM observations revealed that oriented mordenite crystals on a porous support seemingly developed via an "evolutionary selection" mechanism. The conditions under which the "evolutionary selection" process can occur include at least: (a) the high number density of nuclei on the support surface at the early stage; (b) the crystals should grow fastest along one direction; (c) the zeolite layer proceeds by the successive growth of the crystals nucleated on the support instead of the accumulation of the crystals formed in the solution.

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