Microstructure analysis of highly water permeable zeolite MOR membrane

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In recent years, highly water permeable mordenite-type (MOR-type) zeolite films have been attracting attention for use as membranes to separate acetic acid and water [1-3]. In this study, MOR membranes were fabricated using seed crystals under dilute solution conditions. These films show almost no permeation most of molecules apart from water, exhibiting extremely high separation ability. In this study, electron microscopy was used as the primary means of examining the microstructure of the MOR-type zeolite membranes, and the formation mechanism of the film was examined while also revealing the effect of a membrane's structure on its properties.

After affixing seed crystals by dip coating, MOR-type zeolite membranes were grown on porous alumina substrates in a solution of relative formula Na_2O: Al_2O_3 : SiO_2 : H_2O = 10 : 0.15 : 36: 960. MOR membranes were sectioned using ion-milling, and a transmission electron microscope (JEM -3000F, JEOL) and a scanning electron microscope (Hitachi SU-8000) used to observe the cross-sectional structure.

Figure 1 show cross-sectional images of a MOR membrane. The synthesized MOR membrane was observed to be well densified, and allowed only water molecules to pass through, even blocking the passage of hydrogen molecules. The zeolite layer was found to form on the substrate surface as well as in substrate pores. The MOR membrane above the substrate consisted of two regions: a layer that formed immediately above the substrate surface consisting of poorly shaped microcrystals ranging from several 10s of nanometers to 200 nm in size to a thickness of about 1 μm with random crystal orientations, above which a second layer formed with epitaxial crystals grown preferentially in the <001> direction. In the randomly oriented layer, crystal grains a few nanometers in size were connected by an amorphous-like layer. In addition, zeolite grains formed in the pores of the alumina substrate to a depth of a few microns. In the well-oriented region, crystallites were not connected directly to one another, and thus will not contribute to the permeability of the membrane. The so-called active separation layer is thus expected to correspond to the layer with randomly shaped and oriented crystals or the crystals formed within the substrate pores.

In order to elucidate the mechanism of zeolite layer formation the relationship between synthesis time and membrane thickness was examined (Fig. 2). This revealed that the growth rate of the zeolite membranes is nonlinear with time; up to2 h, no growth occurs, but within a short time of 3 to 4 h suddenly growth begins, after which growth continues at a moderate pace. In other words, the film growth thickness follows a classic 'S' shape as a function of time. Based on the results of these experiments, a formation mechanism for the membrane is proposed.

This work was partially financially supported by NEDO, Japan, as part of the research project "Green and sustainable chemistry/fundamental development of ordered-nanoporous membranes for highly-refined separation technology".

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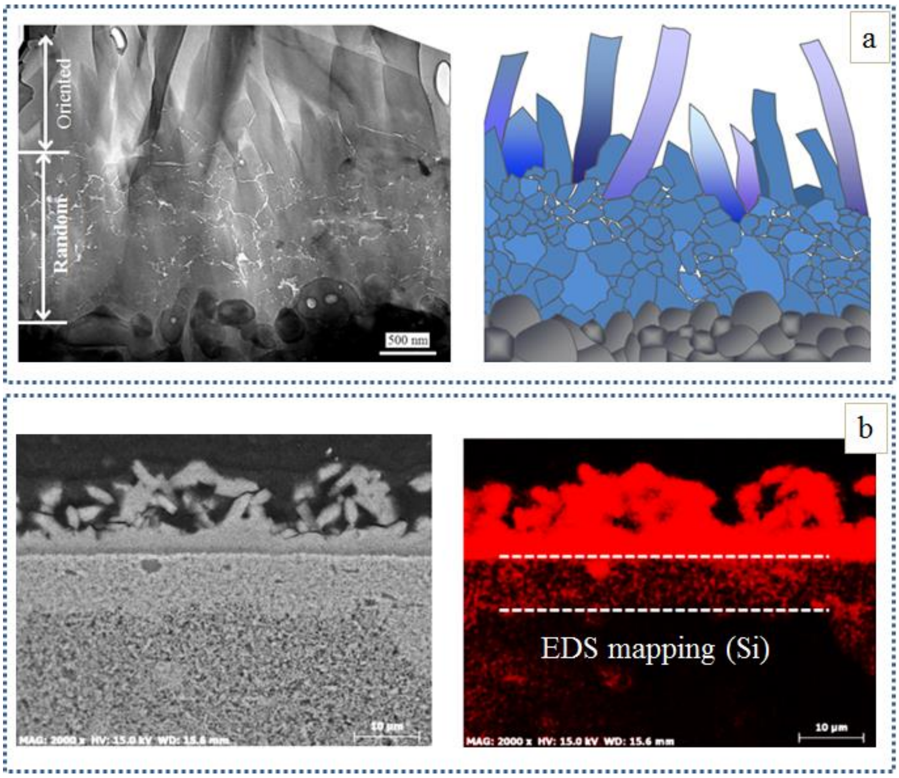

Fig. 1 (a) TEM and (b) SEM and EDS mapping images of the MOR membrane treated for 6 hours.

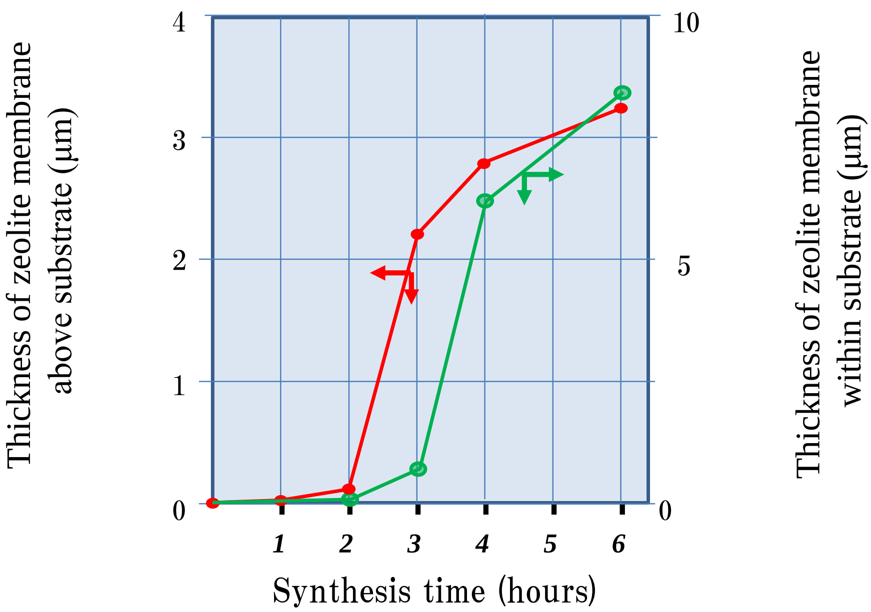

Fig. 2 Relationship between synthesis time and membrane thickness of the zeolite membrane formed on the surface and within pores of the Al_2O_3 substrate.