Electrophoretic deposition of orientation-controlled zeolite L layer on porous ceramic substrate

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Magneto-scientific technique combined with colloidal processing was applied to obtain crystalline-orientation zeolite L seed layers. Well-dispersed non-aqueous suspensions of the zeolite L were prepared for the fabrication of thin seed layers on porous substrates by electrophoretic deposition (EPD) in a superconducting magnet. The c-axis oriented seed layers of the zeolite L was successfully obtained on porous YSZ substrates by EPD under the magnetic field.

Key-words: Zeolite L, Crystalline-orientation, Strong magnetic field, Electrophoretic deposition, Polypyrrole

Zeolites, which are often referred to as molecular sieves, are crystalline aluminosilicates forming three-dimensional frameworks with uniformly-sized pores of molecular dimensions. Zeolites have been well recognized for their unique ability to adsorb and separate gas molecules, catalyze chemical reactions and selectively exchange cations in solutions. The framework types over 200 are listed in the database of the International Zeolite Association, and the structure code which consists of three alphabet capital letters is given to each zeolite. In general, the effect of preferred orientation of crystals on molecular adsorption and transport through zeolite membranes is expected to be significant due to the highly anisotropic pore networks found in many zeolites. Preferred orientation of the crystals can affect not only the diffusion rates through the zeolite layer, but also the density and morphology of the intercrystalline pores. In the case of zeolites which possess a cubic crystalline structure such as zeolite A, however, the effect of preferred orientation on intrinsic diffusion rate through the zeolite is expected to be negligible, since the zeolites have an isotropic pore network with equal diffusion coefficients in all crystal directions.1)

Zeolite L, which is classified as LTL, has a typical composition of KAlSi3O8·nH2O (n = 0–4). The crystal system of zeolite L is classified in the hexagonal group (space group P63/mmm) with the cell dimensions of a = 1.84 nm and c = 0.75 nm, and has an anisotropic pore network: One-dimensional channels running along the c-axis, the aperture size of which is 0.71 nm. Therefore, c-axis orientation is preferable to bring out the best performance of zeolite L. Oriented zeolite L monolayers with dense packing and high coverage degree has been obtained by using a luminescent perylenediimide-bridged silsesquioxane precursor as the novel molecular binder.2) The zeolite L thin films with different orientations has also been fabricated by applying fine zeolite L seed crystals on glass substrates and then hydrothermally treating the seeded substrates in reaction sols. For the film fabricated at a small amount of KOH or at a high hydrothermal temperature, the c-axis of the zeolite crystals was found to be oriented normal to the substrate.3)4)

Our group has studied the magnetic anisotropy of zeolites having crystallographically asymmetric frameworks. Our previous study has disclosed that mordenite with an orthorhombic unit cell has an easy-magnetization axis along the b-axis in the crystals.5) Based on the magnetic orientation theory, the b-axis oriented compacts of mordenite were fabricated in a static magnetic field. We has also demonstrated that the c-axis orientation of mordenite is achieved by using a rotating strong magnetic field.6) This is related to the intrinsic character of mordenite that the b- and c-axes are the easy- and hard-magnetization axes in the crystal, respectively. More recently, we have revealed that the c-axis is the easy-magnetization axis for zeolite L.6) The magnetic orientation process would be widely applicable to other types of non-cubic zeolites.

In this study, the fabrication of c-axis oriented zeolite L thin layer was attempted by electrophoretic deposition (EPD) in a strong magnetic field.7)12) During the process, it is expected that the surface-charged zeolite L particles suspended in a liquid medium are oriented by applying the magnetic field and then manipulated toward a substrate by applying electric field while retaining their orientation. The deposition of the zeolite L particles was performed on porous ceramic substrates aiming a seeding process for the following secondary growth method.

The starting material was commercially-available highly siliceous K+ type zeolite L (HSZ-500KOA, Tosoh Co., Ltd.; SiO2/Al2O3 = 6.1). The size of the 50% cumulative value, D50, corresponding to the mean particle size, was evaluated to be about 0.4 μm for the dispersed powder by dynamic light scattering (ELS-Z2, Otsuka Electronics Co., Ltd.). The powder was dispersed in ethanol by ultrasonic vibration and then the prepared suspension was left for 3 days without stirring to remove agglomerated particles. After the sedimentation classification, only the supernatant was collected as the suspension for the EPD process without adding any acid/base or dispersing agents.

The zeolite L particles were negatively charged in the suspension. Porous ceramic substrates were prepared by low temperature sintering using commercially-available 8 mol% yttria-stabilized zirconia (TZ-8Y, Tosoh Co., Ltd.). The surfaces of the sintered substrates were coated with polypyrrole, a conducting
polymer, to make them electrically conductive. The coating process has been described in detail elsewhere.\textsuperscript{13,14)}

The schematics of the experimental setup are shown in Fig. 1. The EPD was performed in the two directions: (A) upwards: opposing gravity and (B) sideways: perpendicular to gravity. The coated YSZ substrate and stainless steel with a working area of 16 mm were used as the anodic and cathodic electrodes, respectively. The distance between the electrodes was fixed at 20 mm. The EPD was carried out at a constant voltage condition of 200 V using a DC power supply (Model 2400 SourceMeter, Keithley Instruments, Inc., USA). A cryogen-free superconducting magnet with a room temperature bore of 100 mm (JASTEC, Inc., JMTD-12T100NC5) was used to apply a 12 T strong magnetic field during the EPD. The morphology of the obtained deposits was observed using a scanning electron microscope (SEM) (JSM-6500, JEOL). X-ray diffraction (XRD) (Rigaku-2500, Rigaku) with monochromatic Cu-K\(\alpha\) radiation was used to characterize the thickness and crystalline orientation of the deposits.

During the EPD process, the negatively-charged zeolite particles migrated towards the anodic substrate and deposited there. Figures 2(A) and 2(B) show the XRD patterns of the zeolite L layer deposited on the YSZ substrates without applying magnetic field. The deposition directions against the gravity are different between (A) upwards deposition and (B) sideways deposition. The increase in the XRD intensity indirectly shows the increase in the deposit yield with time. Similar peak patterns showing random orientation were observed in both (A) and (B). The Lotgering factor,\textsuperscript{15)} which is often used as an index showing the degree of orientation, calculated for both the XRD patterns (A)(f) and (B)(f) was \(F = 0.00\). This means that the direction of the gravity does not affect the orientation of the particles. From the comparison of the general peak heights between (A) and (B), higher deposition rate was observed in the sideways deposition against the gravity.

Figure 3 shows the surface appearance of the deposits after the deposition for 5 and 10 min. In the case of sideways deposition against the gravity, many large agglomerates are observed on the substrates. This tendency could not be eliminated even by lowering the applied voltage. Homogeneous deposits were obtained in the upwards deposition against the gravity. Similar deposition experiments were also performed downwards, however, the quality of the deposits was the worst (not shown here). Therefore, we decided to adopt the upwards deposition against the gravity.

Figure 4 shows the XRD patterns of the zeolite L on the YSZ substrates in a 12 T strong magnetic field. The direction of the magnetic field was parallel to the deposition direction (vertically upwards). The deposition time was fixed to be 10 min. For comparison, the XRD patterns of the as-received powder and a deposit obtained without applying the magnetic field are shown in this figure. The XRD pattern of the zeolite L layer deposited without applying magnetic field shows that the layer has random orientation. On the other hand, the XRD pattern of the zeolite layer deposited in the vertically applied static magnetic field, which is perpendicular to the substrate, shows different characteristics from random orientation. We have reported that the easy
magnetization axis of zeolite L is the c-axis. Therefore, the peak intensity from the (001) plane was obviously high. The Lotgering factor, an index showing the degree of orientation, was $F = 0.17$ for the deposit prepared in a 12 T magnetic field. However, the degree of orientation for the thin layers prepared on porous substrates was inferior to that of thick deposits prepared by slip casting. To date, we have not obtained highly-oriented thin layers prepared on porous substrates because the deposition direction (vertically upwards). Another possible reason is the contamination of very fine agglomerated particles with random orientation in the deposit which was not prevented even by the upward deposition.

**Figure 5** shows the surface appearance and SEM images of the deposited layer on the YSZ substrate by EPD in the magnetic field. Homogeneous deposit was also obtained in the magnetic field. The SEM image shows many hockey-puck-like particles are oriented, the flat faces of which are in an upward direction. The thickness-controlled layers were obtained with controlled deposition time. The thickness of the layer could be controlled with the applied voltage; however, it was observed that the lower applied voltages made the deposit surface inhomogeneous and the higher applied voltages made the control of the deposit thickness very difficult. In the present work, the applied voltage of 200 V could produce homogeneous, thickness-controlled layers with the c-axis orientation for the zeolite L. The thickness of the deposit layer prepared at 200 V for 10 min was approximately 3 μm.

In summary, EPD technique was applied to the seeding process of zeolite L on porous YSZ substrates. Homogeneous deposit layers were obtained by the upwards deposition against the gravity using stable suspension. The c-axis orientated zeolite L thin layer could be obtained by EPD in a 12 T strong magnetic field. It should be added that the polyvinylpyrrolidone film can be removed by the thermal treatment at 500°C in air without collapsing the deposited structure. We are now preparing zeolite L membranes by the secondary growth method using the oriented seed-applied porous YSZ substrates.

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**References**

1) “Handbook of Zeolite Science and Technology”, S. M. Auerbach, K. A. Carrado and P. K. Dutta, CRC Press (2003) p. 876.
2) H. Li, Y. Wang, W. Zhang, B. Liu and G. Calzaferri, *Chem. Commun.* (Camb.), 2853–2854 (2007).
3) T. Ban, J. Morimoto and Y. Ohya, *Mater. Chem. Phys.*, 109, 347–351 (2008).
4) C. Matsunaga, T. Uchikoshi, T. S. Suzuki, Y. Sakka and M. Matsuda, *Chem. Lett.*, 39, 347–349 (2010).
5) C. Matsunaga, T. Uchikoshi, T. S. Suzuki, Y. Sakka and M. Matsuda, *Microporous Mesoporous Mater.*, 151, 188–194 (2012).
6) C. Matsunaga, T. Uchikoshi, T. S. Suzuki, Y. Sakka and M. Matsuda, *Mater. Lett.* (accepted).
7) T. Uchikoshi, T. S. Suzuki, H. Okuyama and Y. Sakka, *J. Mater. Res.*, 18, 254–256 (2003).
8) T. Uchikoshi, T. S. Suzuki, H. Okuyama and Y. Sakka, *J. Mater. Res.*, 19, 1487–1491 (2004).
9) T. Uchikoshi, T. S. Suzuki, H. Okuyama and Y. Sakka, *J. Mater. Sci.*, 39, 861–865 (2004).
10) T. Uchikoshi, T. S. Suzuki and Y. Sakka, *J. Mater. Sci.*, 41, 8074–8078 (2006).
11) T. Uchikoshi, T. S. Suzuki, S. Imura, F. Tang and Y. Sakka, *J. Eur. Ceram. Soc.*, 26, 559–563 (2006).
12) T. Uchikoshi, T. S. Suzuki and Y. Sakka, *J. Eur. Ceram. Soc.*, 30, 1171–1175 (2010).
13) T. Uchikoshi, S. Furumi, T. S. Suzuki and Y. Sakka, *J. Ceram. Soc. Japan*, 114, 55–58 (2006).
14) L. Kreethawate, S. Larpkiattaworn, S. Jemsrihlera, L. Besra and T. Uchikoshi, *Surf. Coat. Tech.*, 205, 1922–1928 (2010).
15) F. K. Lotgering, *J. Inorg. Nucl. Chem.*, 9, 113–123 (1959).
16) C. Matsunaga, T. Uchikoshi, T. S. Suzuki, Y. Sakka and M. Matsuda, *J. Ceram. Soc. Japan*, submitted.
17) T. Uchikoshi and M. Matsuda, *Chem. Ind.*, 62, 697–700 (2011) [in Japanese].