

Zeolite coating on foamed stainless steel by in-situ crystallization method

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Abstract Faujasite-type zeolite films were prepared on foamed stainless steel by the in-situ crystallization method. Precursor solutions were prepared by dissolving water glass and NaAlO_2 in a NaOH solution and aged at room temperature for two days. The concentrations of the starting materials were varied from 0.29 to 2.3 M (in SiO_2 concentration) keeping the molar ratios of $\text{Na}_2\text{O}:\text{SiO}_2:\text{Al}_2\text{O}_3$ fixed at 3.6:3.0:1.0. The foamed stainless steel substrate had about 90% of porosity and an average pore size of 600 μm . It was dip-coated in the precursor solution four times, then hydrothermally treated at 80°, 110° and 150°C for 6–48 h. The XRD patterns and SEM photographs revealed that faujasite-type zeolite was formed predominantly at a SiO_2 concentration of 1.1 M, temperature of 110°C and duration of 24 h, with a product particle size of 2–5 μm . At higher concentrations of the precursor solution, hydroxylsodalite becomes the major product rather than faujasite-type zeolite. The adherence strength of the zeolite grains deposited on the foamed stainless steel is higher in the in-situ crystallization method than when a conventional solution method is used. Thus, the in-situ crystallization method is concluded to be effective for preparing zeolite films even on metal substrates.

Keywords Zeolite coating · Foamed stainless steel · In situ crystallization · Faujasite-type zeolite · Hydrothermal treatment

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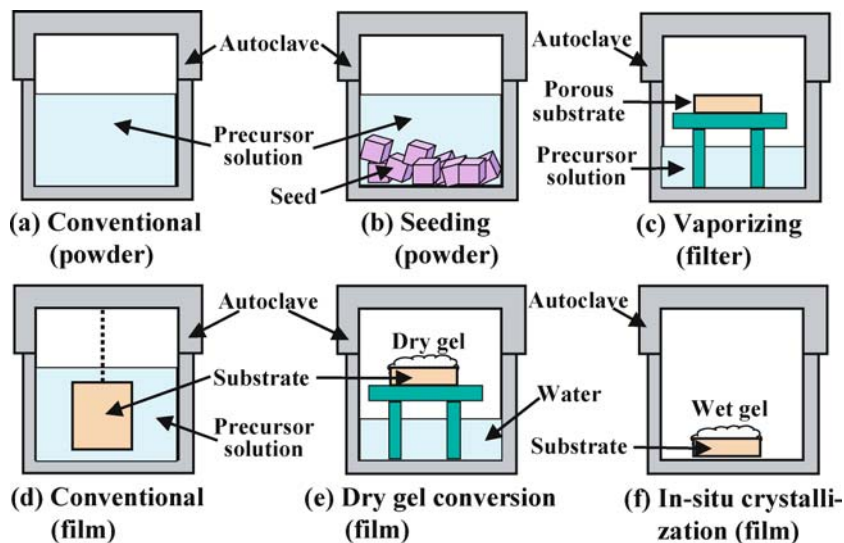
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1 Introduction

Zeolites are functional materials used as catalysts, catalyst supports, ion exchangers, adsorbents, etc. It is preferable to use zeolites as films rather than in the more generally used form of pellets, to enhance the target chemical reactions. Zeolite films are generally prepared by a solution process using hydrothermal reaction of an aluminosilicate solution containing a strong alkali solution. The conventional solution method has, however, the disadvantage of degrading the substrate in the strongly alkaline conditions. The preparation methods [1–4] shown schematically in Fig. 1 are therefore proposed to avoid this. To produce zeolite coatings on substrates, three methods (Fig. 1(d)–(f)) have been reported. To avoid substrate degradation, the dry gel conversion method (Fig. 1(e)) [5] and the in-situ crystallization method (Fig. 1(f)) [6, 7] are better than the conventional method (Fig. 1(d)) [4]. The in-situ crystallization method of depositing a precursor gel by spin coating or dip coating of the precursor solution on the substrate and crystallizing it under hydrothermal conditions utilizing the residual moisture has the advantage of converting the precursor gel to zeolite at lower hydrothermal temperatures.

We have reported the preparation of ZSM-5 zeolite (which has a high molecular sieving function) as a coating on cordierite honeycombs by the in situ crystallization method [6, 7]. The ZSM-5 crystal grains formed on the substrates with a thickness of 20 μm adhered well to the substrate because the precursor gel reacts with the substrate at the interface. The Si/Al ratio of the ZSM-5 coating was thus tuned by the chemical composition of the substrate, which can be controlled by selective acid leaching. The resulting zeolite coatings consist of equiaxed ZSM-5 crystals about 1–2 μm in size and are porous, containing intergrain macropores. This microstructure enhances chemical reactions because the zeolite

Fig. 1 Schematical depiction of six preparation methods for zeolite and zeolite films



grains inside the coating participate in catalytic and adsorptive reactions within the macropores. We also succeeded in preparing zeolite A (which has the highest cation exchange property of all zeolites) as coatings on honeycombs by the in-situ crystallization method [7].

Compared with zeolite coatings on ceramic substrates, the adherence strength of zeolite coatings on metal substrates is weak, due to the lack of reaction between the zeolite grains and the metal substrate. To improve the adherence, Coutinho and Balkus Jr [8] used a pulsed-laser deposition method, which, however cannot be applied to the complex shaped substrates (honeycombs, foams, meshes, etc.), which are the preferable shapes for catalytic and adsorptive applications.

From the above, it is highly desirable to develop zeolite coatings with improved adherence strength between the zeolite crystal grains and the metal substrate. In this paper, a faujasite-type zeolite was coated on foamed stainless steel using the in-situ crystallization method and the adherence strength was compared with that of samples prepared by a conventional solution method.

2 Experimental

The substrates were foamed stainless steel (SUS316) with a porosity of about 95 vol% and an average pore size of 600 μm (Mitsubishi Materials, Japan). $4 \times 1 \times 0.2 \text{ cm}^3$ slabs were cut from the foamed stainless steel and used as substrates. Precursor solutions were prepared by mixing water glass ($\text{Na}_2\text{O} \cdot 2.2\text{SiO}_2 \cdot 8.8\text{H}_2\text{O}$) and NaAlO_2 in NaOH solution. All the chemicals were from Wako Pure Chemicals, Japan. The molar ratios were $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{H}_2\text{O} = 3:1:1.8:x$, where $x = 78, 114, 150, 222, 438$ and 582 , corresponding to SiO_2 concentrations of 2.1, 1.5, 1.1, 0.6, 0.4 and

0.3, respectively. The adopted Si/Al ratio is the same as for the standard synthesis of zeolite X ($\text{Na}_x[\text{Al}_x\text{SiO}_{1+x}]2.5\text{H}_2\text{O}$, $x \cong 2/3-1$), which has a lower Si/Al ratio than zeolite Y ($\text{Na}_x[\text{Al}_x\text{SiO}_{1+x}]2.5\text{H}_2\text{O}$, $x \cong 1/3-2/3$) but the same faujasite-type structure [9]. The cloudy precursor solutions and were aged for 2 days with slow stirring to ended the hydrolysis of the SiO_2 component to form nano-clusters with a framework structure of $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra [9].

The flowchart for the preparation of zeolite-coated samples by the in-situ crystallization method is shown in Fig. 2. The substrates were dipped in the precursor solutions four times. After dipping, sample A was prepared by direct hydrothermal treatment of the dipped sample in a Teflon lined autoclave. By contrast, sample B was prepared by absorbing the excess water from the dipped sample using filter paper before hydrothermal treatment while sample C was prepared by partially drying the deposited wet precursor

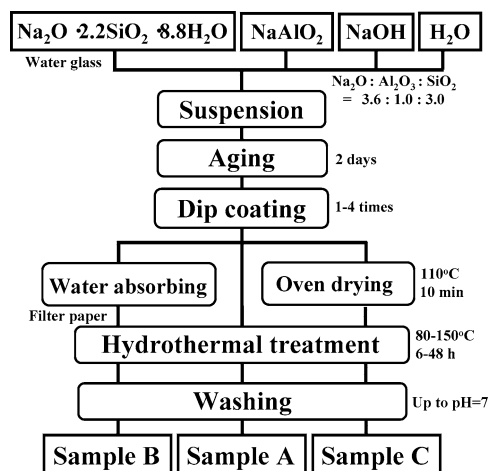


Fig. 2 Flowchart for the preparation of zeolite-coated samples by the in-situ crystallization method

gel at 110°C for 10 min in an oven. These hydrothermal treatments were performed using an 25 ml autoclave at 80°, 110° and 150°C for 6–48 h. After the hydrothermal treatments, the samples were washed with distilled water until the pH of the washed solution became about 7. Ultrasonic treatments were performed in an ultrasonic bath for 10 min to determine the adherence strength of the deposited zeolite grains. The amount of deposited coating, both before and after washing, and after the washing-ultrasonic treatments was determined by weighing the samples.

The crystalline phases formed in the products were investigated by powder X-ray diffraction (XRD; LabX XRD6100, Shimadzu, Japan). The microstructures of the samples were observed using a scanning electron microscope (SEM; S-2050, Hitachi, Japan) at an accelerating voltage of 20 kV. The cross section of the coated sample was examined by electron probe microanalysis (EPMA; JXA-8200, JEOL, Japan) after impregnating the sample in resin.

3 Results and discussion

3.1 In-situ crystallization method

As mentioned above, samples were prepared using three different drying conditions after hydrothermal treatment at 110°C for 24 h. After washing, the resulting samples were investigated by XRD. The formation of faujasite-type zeolite was confirmed in samples A and B but not in C, in which the residual water content in the precursor gel was insufficient to form zeolite (a hydrate phase). The XRD peak intensities of the product zeolites in sample B were stronger than those of sample A. Absorbing the excess water from the deposited precursor gel is thus effective in facilitating zeolite formation on the substrate. This may result from the more intimate contact of the precursor gel with the substrate achieved by removing the excess water. All the samples were prepared by this method.

The effect of precursor gel concentration on zeolite formation was investigated by changing the concentrations from 0.3 to 2.1 M SiO₂. XRD measurements were performed on both the as-prepared and washed samples. The XRD patterns of the as-prepared samples show only weak peaks while those of the washed samples show clearer peaks. Thus, the as-prepared samples appear to contain a considerable amount of amorphous phase in addition to the crystalline phase and it is necessary to remove the amorphous phase by washing. The XRD patterns of the washed samples are shown in Fig. 3. Formation of faujasite-type zeolite is observed in all the samples prepared at precursor concentrations of 0.6 to 2.1 M. Small peaks were observed in the samples prepared from 0.3 and 0.4 M solutions due to the small amount of coating formed by the low initial precursor concentrations. The sample prepared

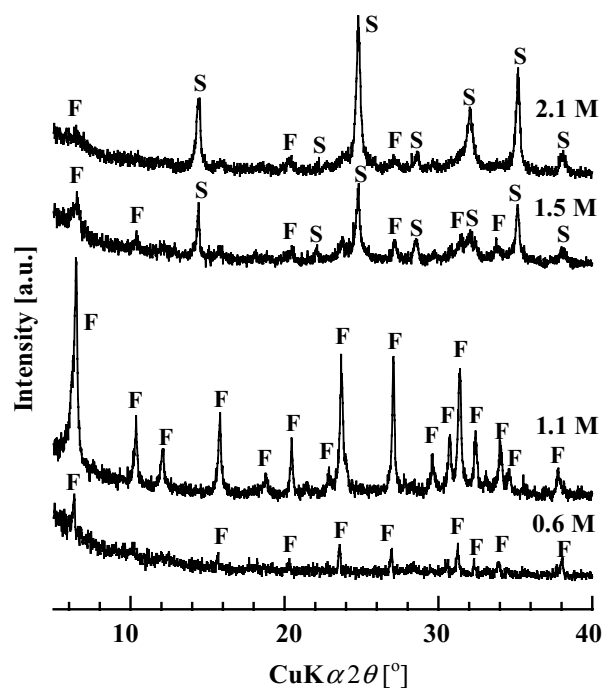


Fig. 3 XRD patterns of zeolite-coated samples prepared from various precursor concentrations (SiO₂ concentration). *F* = faujasite-type zeolite and *S* = hydroxylsodalite

from 1.1 M solution shows much stronger peaks than the other samples. Other peaks unassigned as zeolite observed in the samples prepared from 1.5 and 2.1 M solutions are due to hydroxylsodalite [1]. This phase does not belong to the zeolite group but to a zeolite-related group. The crystal structure of hydroxylsodalite (Na₈[Al₆Si₆O₂₄](OH)₂) consists of simple cubic packing of 14-faced forms (truncated octahedra), built by corner-shared (Si,Al)O₄ tetrahedra. Na⁺ and OH⁻ ions occupy the cavities present inside the 14-faced forms. Thus, the structure unit of the 14-faced form of hydroxylsodalite is in common with faujasite-type zeolite, in which structural 14-faced forms are packed in a face-centered lattice with a large space called a super cage at the center of the lattice. The formation of faujasite-type zeolite and hydroxylsodalite in the coatings is plotted in Fig. 4 as a function of precursor concentration. The product phases are found to change from faujasite-type zeolite to hydroxylsodalite at higher precursor concentrations. SEM photographs of the product faujasite-type zeolite and hydroxylsodalite particles are shown in Fig. 5. The faujasite-type zeolite particles are 2–5 μm in size with an equiaxed shape consisting of many small planes with convex angles due to penetration twinning. By contrast, the hydroxylsodalite particles are much larger (10–20 μm in size) with a spherical shape consisting of aggregations of many small grains with penetration twinning. The formation mechanisms for the phases are, thus, thought to proceed as follows; formation of nano-clusters built by corner-shared (Si,Al)O₄ tetrahedra → formation of

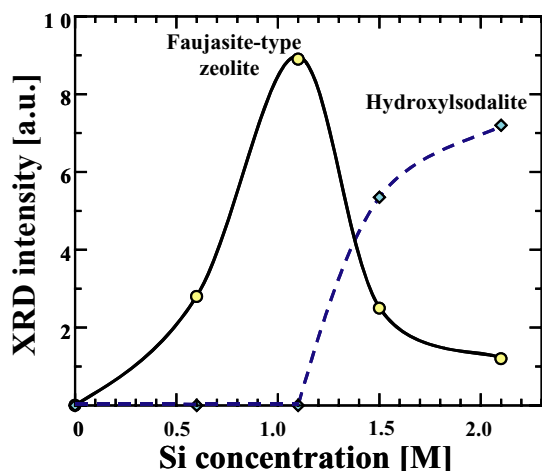


Fig. 4 Formation curves of faujasite-type zeolite and hydroxylsodalite as a function of precursor solution concentration

structural units of 14-faced forms \rightarrow their loose packing to form faujasite-type zeolite with large spaces in the structure \rightarrow denser packing to form hydroxylsodalite. Since such phase changes are also observed with higher-temperature hydrothermal treatment and longer treatment times [4, 10], this is thought to correspond to a change from a metastable to a stable phase.

The effects of hydrothermal temperature and reaction time were also investigated by changing these experimental conditions using a precursor solution concentration of 1.1 M. The XRD peaks of faujasite-type zeolite were the most intense in the sample prepared at 110°C and drastically decreased in intensity at 150°C. The best hydrothermal temperature is found to be 110°C. Using this hydrothermal temperature, the effect of changing the reaction time from 6 to 48 h was examined. The XRD peaks of faujasite-type zeolite were the highest in the sample reacted for 24 h and decreased at both shorter and longer reaction times. The best reaction time is, therefore, 24 h. To summarize, the optimal experimental conditions to obtain the highest amount of faujasite-type zeolite

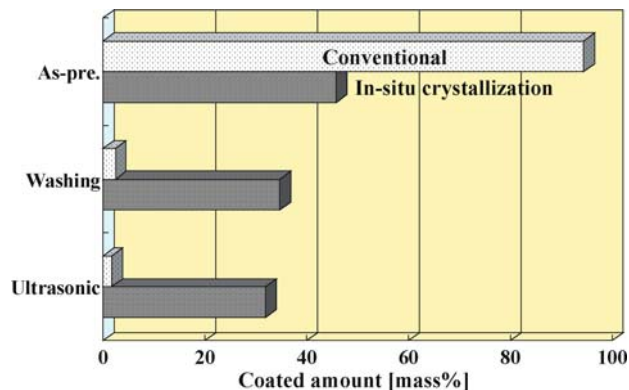


Fig. 6 Changes in the amount of coating on samples as-prepared, after washing and washing-ultrasonic treatments by the conventional and in-situ crystallization methods

are as follows; concentration of precursor solution = 1.1 M, hydrothermal temperature = 110°C and reaction time = 24 h.

3.2 Adherence strength of the zeolite products

The adherence strength of the product zeolite grains to the substrate was evaluated from the weight loss of the coating after washing and washing-ultrasonic treatments, of samples prepared both by in-situ crystallization and conventional methods. The results for both samples are shown in Fig. 6. The amount of coating initially formed on the conventional sample is almost twice that on the in-situ crystallization sample. However, the amount of coating of the conventional sample decreases drastically after washing, i.e. only 2.5% is retained. By contrast, the amount of coating on the in-situ crystallization sample falls to only 76% after the washing treatment, reflecting the difference of adherence strength of the zeolite grains prepared by the two methods. SEM photographs before and after the washing treatment for both samples are shown in Fig. 7. The photographs clearly show that almost all of the surface grains on the foamed stainless steel have disappeared after washing the conventional sample. On the other hand, the washed in-situ crystallization

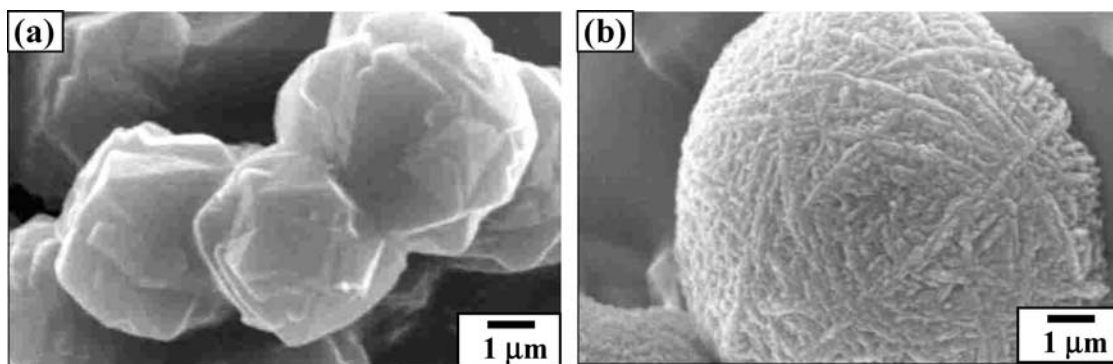


Fig. 5 SEM photographs of faujasite-type zeolite (a) and hydroxylsodalite (b)

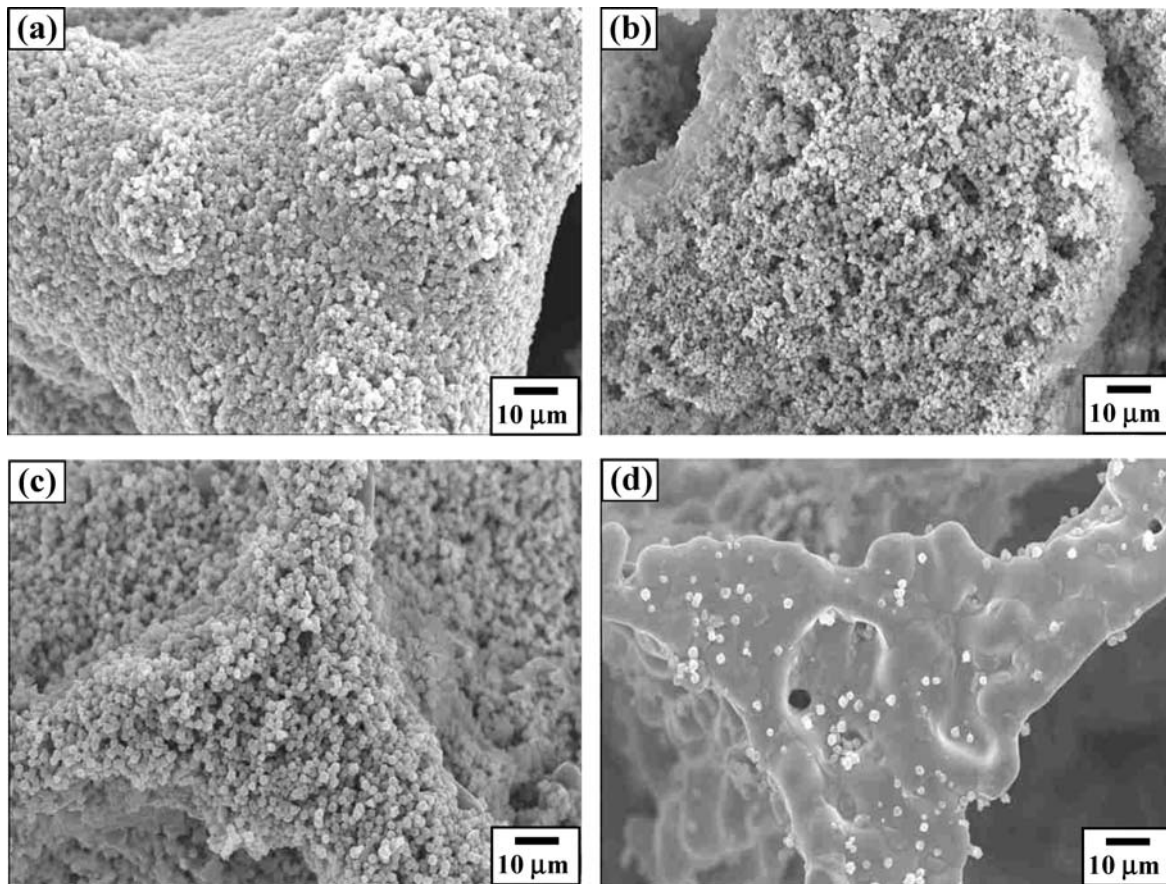


Fig. 7 SEM photographs of samples prepared by the in-situ crystallization method, as-prepared (a) and after washing (b), and by the conventional method, as-prepared (c) and after washing (d)

sample retains many zeolite grains on the substrate surfaces. This great difference is thought to be due to the difference in the adherence strength of the zeolite grains because the zeolite nuclei are in intimate contact with the substrate in the in-situ crystallization method by direct deposition of the precursor on the substrate. In the conventional method, the zeolite nuclei are thought to be formed not only on the substrate (by heterogeneous nucleation) but also in the solution (formed by homogeneous nucleation). In the in-situ crystallization sample, 70% of the product zeolite grains in the as-prepared sample are retained on the substrate even after the washing-ultrasonic treatment. This amount of retained coating on the in-situ crystallization sample is 20 times higher than in the case of the conventional sample. EPMA analysis of the cross-section of this in-situ crystallization sample reveals that coating occurs inside the foamed stainless steel substrate with rather thicker layers formed inside the sample.

Mabande et al. [11] and Bonaccorsi and Proverbio [12] successfully prepared ZSM-5 and zeolite A coatings on stainless steel after thermal oxidation and/or alkali surface treatments. This suggests that such surface treatments are

effective in enhancing the adherence strength of the zeolite grains formed on the present foamed stainless steel substrate.

4 Conclusion

Coatings of faujasite-type zeolite on foamed stainless steel were produced using the in-situ crystallization method and the adherence strength of the product zeolite grains was compared with those formed by a conventional solution method. In the in-situ crystallization method, the residual water content of the precursor gel was an important factor in the crystallization of the zeolite. Removal of the excess water from the deposited precursor gel before hydrothermal treatment was found to facilitate the process. The optimal conditions to form a zeolite coating are a precursor solution containing 1.1 M SiO₂, a hydrothermal temperature of 110°C and a reaction time of 24 h. The adherence strength of the formed zeolite grains prepared by the in-situ crystallization method was clearly higher than in the product formed by a conventional solution method.

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