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## Preparation of zeolite-coated cordierite honeycombs prepared by an in situ crystallization method

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### Abstract

Zeolite thin films were prepared on cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ) honeycomb substrates by in situ crystallization using soft hydrothermal conditions. The synthesized zeolite films (zeolite A and ZSM-5) were characterized by XRD, FTIR, SEM,  $\text{NH}_3$ -TPD, and  $\text{N}_2$  and propane gas adsorption. Zeolite-A films were prepared by dip-coating on a cordierite substrate in a precursor of molar composition of  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O} = 4:1:2:100$  and heating in an autoclave at  $80^\circ\text{C}$  for 6–10 h. The resultant zeolite-A films consisted of cubic crystals about 2–3  $\mu\text{m}$  in size, achieving a thickness of 20  $\mu\text{m}$  after re-coating. ZSM-5 films were similarly formed using a microporous silica precursor obtained by selective leaching of metakaolinite with tetrapropylammonium hydroxide (TPAOH) as the templating agent. The molar composition of the precursor was  $\text{NaOH}:\text{microporous silica}:\text{TPAOH}:\text{H}_2\text{O} = 1:10:1:200$ . The dipped substrate covered with the wet precursor gel was heated in an autoclave at  $150^\circ\text{C}$  for 24 h. The resultant films were composed of short prismatic  $< 1 \mu\text{m}$  crystals achieving thickness of several to 10  $\mu\text{m}$  after re-coating. The microstructure and porous properties of the ZSM-5 films were found to change according to the chemical composition and surface treatment of the cordierite substrates. The presence of a  $\text{SiO}_2$ -rich interfacial layer between the substrate and zeolite film increased the amount of zeolite formed and the physical adsorption but decreased the solid acidity and amount of chemisorption.

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**Keywords:** Zeolite films; In situ crystallization; Porous properties; Microstructure; Hydrothermal treatment

### 1. Introduction

Zeolites are unique crystalline compounds containing uniform sized micropores in their crystal structures. They show excellent cation exchange capacities, strong solid acidities, high adsorbing abilities, molecular sieving properties, and so on [1]. Since these properties are related to their surface chemical reactions, it is much more effective to increase the concentration of reaction sites over those of bulk zeolites by preparing films and/or membranes. Many works have therefore been reported on the preparation of zeolite films and membranes [2]. Although many zeolites have been synthesized [3], only a few, i.e. faujasite-type zeolites (A, Y and X) and high-silica zeolites (ZSM series) are used commercially. In this connection, zeolite films coated on multi-channel honeycomb monoliths have the advantage of high geometric surface areas resulting in more active zeolite

surfaces and large open frontal areas giving superior permittivity for reactions in the gas phase and in solution.

Zeolites are generally synthesized under hydrothermal conditions, i.e. crystallized from a solution containing  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  with optional templates or seeds. Zeolite films have been also prepared by hydrothermal treatment of a substrate dipped into a precursor solution. In such preparations, the zeolite precursor dissolves in the solution but the resulting zeolite particles do not adhere to the substrate. In situ zeolite film formation has been reported by Okada et al. [4,5] and Katsuki et al. [6]. Okada et al. reacted a  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  glass fiber net with NaOH solution in an autoclave and succeeded in preparing zeolite A-[4] and zeolite X-coated fibers [5] by surface dissolution of the glass fibers followed by deposition of zeolites by an in situ reaction with the NaOH solution. Katsuki et al. [6] reacted mullite/glass composite honeycombs with NaOH solution and prepared ZSM-5 coated honeycombs in situ. In situ reaction has the advantage of producing strongly adhering zeolite coatings on the substrates but a disadvantage is the degradation of the mechanical strength of the substrates resulting from the long reaction times.

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Zeolite ceramics [7,8] and honeycombs [9] have also been prepared for applications such as deodorant materials and adsorbents. Kato [7] prepared zeolite A and mordenite honeycomb monoliths by a conventional sintering method using zeolite powder with fibers and binders. Madhusoodana et al. [9] prepared ZSM-5 zeolite disk ceramics by in situ crystallization using a wet gel precursor with a small amount of added glass fiber to assist forming. In this preparation, a green pellet formed from a dry precursor gel containing dispersed glass fibers was converted to a zeolite ceramic by dry heating in an autoclave. The moisture in the gel produced a soft hydrothermal condition in the autoclave, forming ZSM-5 zeolite. Although zeolite monoliths have the advantage of high zeolite content, their mechanical strengths are poor due to limitations in their sintering temperatures.

From the above considerations, it is highly desirable to develop zeolite-coated materials with improved adherence between the zeolite film and substrate. This paper describes the preparation of zeolite films on cordierite substrates by an in situ crystallization method and the characterization of the properties of the resultant films.

## 2. Experimental

The substrates were cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ) honeycomb monoliths with a cell density of 400 cells per square inch and a wall thickness of 0.17 mm (BHEL, India). The open porosity was 35% and more than 90% of the pores were 0.5–5  $\mu\text{m}$  in size. Cubes of 1 cm side were cut from the honeycomb monolith and used as substrates. Some of these samples were leached with 10 mass%  $\text{H}_2\text{SO}_4$  at 70 °C for 3 and 6 h to produce a silica-rich surface. All the samples were cleaned with distilled water in an ultrasonic bath for 1 h and then dried at 110 °C overnight.

Metakaolinite ( $\text{Al}_2\text{Si}_2\text{O}_7$ ) prepared by calcining kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ; Albion, GA, USA) at 800 °C for 4 h was mixed with NaOH solution for 12 h to produce a molar composition of  $\text{Al}_2\text{O}_3:\text{SiO}_2:\text{Na}_2\text{O}:\text{H}_2\text{O} = 1:2:4:100$ . The substrates were dipped in the mixture and aged overnight. The dipped substrate was heated in a Teflon-lined autoclave placed in an electric oven at 80 °C for 6–10 h.

Microporous silica was prepared by selective leaching from metakaolinite which had been calcined at 600 °C for 24 h [10]. The calcined clay was treated with 20 mass%  $\text{H}_2\text{SO}_4$  (2.5 M) at 90 °C for 2 and 6 h with stirring, washed with dilute  $\text{H}_2\text{SO}_4$  (0.5 M) and three times with deionized water before filtering. The microporous silica thus obtained had  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 70 and 700. The zeolite precursor was prepared by mixing these microporous silica powders with water, tetrapropylammonium hydroxide (TPAOH; Wako Chemicals, Japan) and NaOH in the molar ratio  $\text{NaOH}:\text{SiO}_2:\text{TPAOH}:\text{H}_2\text{O} = 1:10:1:200$ . A precursor solution with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (molar ratio) = 100 was also prepared from tetraethylorthosilicate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), aluminum tri-*sec*-butoxide ( $\text{Al}(\text{OC}_4\text{H}_9)_3$ ) and TPAOH in a molar ratio  $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{TPAOH} = 100:1:10$ . The solution was stirred

for 12 h then aged overnight. The substrate samples were dipped in the precursor solution during aging, removed from the solution and the excess removed by careful air blowing. The dried samples were heated in a Teflon lined autoclave with a small amount of water at 150 °C for 24 h.

After the hydrothermal treatments, all the samples were washed with distilled water in an ultrasonic bath for 10 min to remove any loosely adhering coating, especially in the corners of the honeycomb, and dried at 110 °C for 1 day. The ZSM-5 samples were calcined at 600 °C for 2 h to remove the template ions.

The formation of zeolite film on the samples was confirmed by powder X-ray diffraction (XRD; Geigerflex, Rigaku, Japan and LabX XRD6100, Shimadzu, Japan). Fourier-transformed infrared (FTIR) absorption spectra were measured by the KBr method using an FTIR spectrometer (FTIR 8200PC, Shimadzu, Japan). The microstructure of the zeolite film deposited on the honeycomb substrate was observed using a scanning electron microscope (SEM; S-2050, Hitachi, Japan and JSM5310, JEOL, Japan). The chemical compositions of the substrates and zeolite films were measured by X-ray fluorescence (RIX2000, Rigaku, Japan) and energy dispersive X-ray spectrometer (EDX) attached to an SEM (SED8600, Seiko EG&G, Japan). The porous properties were determined from  $\text{N}_2$  gas adsorption and desorption isotherms measured at 77 K using an Autosorb-I instrument (Quantachrome, USA). The specific surface area (SSA) was calculated by the BET method [11], the pore size distribution was calculated by the BJH method [11] and the pore volume was obtained from the maximum adsorption at a relative pressure of 0.999. The micropore volume and micropore surface area were calculated using the *t*-plot method [11]. The  $\text{NH}_3$  temperature programmed desorption (TPD) spectra were measured using a TPD-65 instrument (Bel Japan, Japan). The measurements were performed under the conditions proposed by the Committee on Reference Catalyst of the Japan Catalyst Society [12]. Adsorption of propane gas was also measured under the same conditions as the  $\text{NH}_3$ -TPD spectra measurements.

## 3. Results and discussion

### 3.1. In situ crystallization method

Schematic illustrations of the experimental set up for the conventional reaction, dry gel conversion [13] and in situ

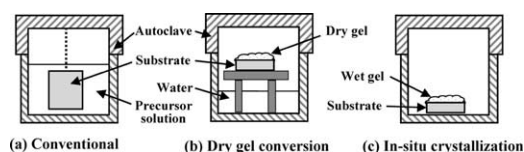


Fig. 1. Schematic illustration of three synthesis methods. (a) conventional, (b) dry gel conversion, (c) in situ crystallization.

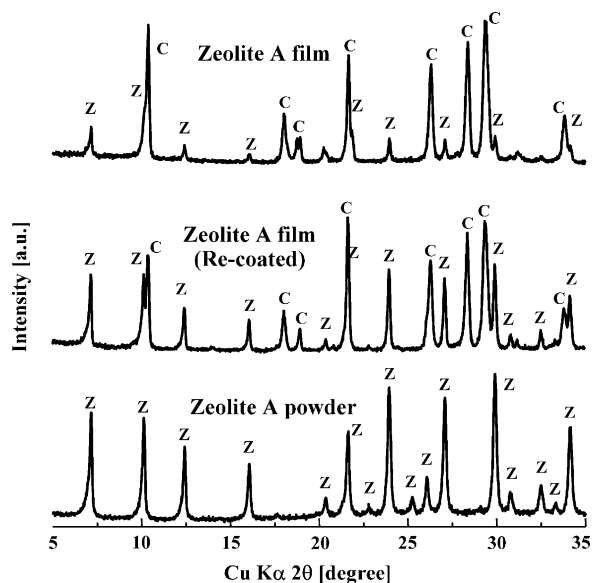


Fig. 2. XRD patterns of zeolite-A film sample obtained by single coating of precursor wet gel and heated at 80 °C for 10 h in an autoclave, zeolite A film sample re-coated and similarly hydrothermally treated, and zeolite A powder sample. Z: zeolite A and C: cordierite (substrate).

crystallization methods are shown in Fig. 1. The conventional method involves the full immersion of the substrate in the precursor solution. In the case of the dry gel conversion method, the dry gel is deposited on the substrate, which is set out of contact with the water in an autoclave vessel. By contrast, in the in situ crystallization method, the wet precursor gel is deposited on a substrate, which is set in the autoclave without additional solution. Since the synthesis of zeolites by the conventional method is generally performed using strong alkali solution, mechanical strength of the substrate tends to be degraded. The weak adherence of the resultant zeolite films on the substrate is also a problem. Comparison of the dry gel conversion and the present in situ crystallization methods shows our preparation method to have the following advantages; (1) greater strength between the zeolite film and substrate because of a chemical reaction occurring during hydrothermal synthesis, (2) the possibility

of synthesis at lower temperatures and (3) a simpler experimental set-up.

### 3.2. Zeolite a coated sample

Zeolite-A films were formed by soft hydrothermal treatment at 80 °C for 10 h. Fig. 2 shows the XRD patterns of the zeolite-A films on cordierite honeycombs. The XRD peak intensities of zeolite A increase after repeated coating (b) because of greater surface coverage and increased amount of zeolite formation. The amount of zeolite A formed after re-coating is about 20 mass%. The FTIR spectra show absorption bands at 466, 554, 664 and 1000  $\text{cm}^{-1}$ , in agreement with zeolite A [14]. The microstructure of the zeolite film formed on the substrate is shown in Fig. 3. A zeolite layer about 15–30  $\mu\text{m}$  thick is observed on the honeycomb cells. The zeolite A crystals constituting the film are cubic in shape with uniform sizes of about 2–3  $\mu\text{m}$ . Observed are many macropores between the crystals and aggregates, resulting from discontinuities in the film due to the rough surface and the presence of non-uniform macropores on the surface of honeycomb substrate. We consider these pores work to enhance the speed of adsorption and the catalytic reactions on the inner part of the deposited film. Repeated in situ crystallization both improved the film continuity and increased its thickness.

The mechanism of zeolite-A film formation may be understood in terms of the following steps; dissolution of the distorted metakaolinite structure by the hydroxyl anion, saturation of the pores and surfaces of the porous substrate with resulting gel and crystallization on the substrate. The kinetics of zeolite A formation depend on the crystallinity of the clay, its calcination temperature, the concentration of alkali and the reaction temperature and time [15]. Since metakaolinite is amorphous, dissolution rates are high, leading to relatively fast zeolite A formation. Microwave heating is very effective to further increase the formation rate. Zeolite film formation is expected to be enhanced by the combined thermal and microwave effects [16].

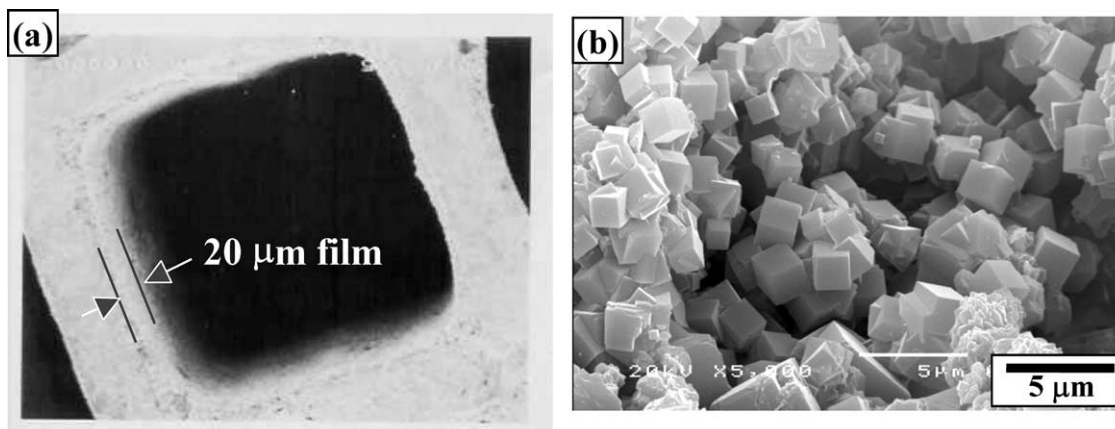


Fig. 3. SEM photographs of zeolite-A film re-coated on cordierite substrate; (a) honeycomb cell, (b) surface of the zeolite A crystals.

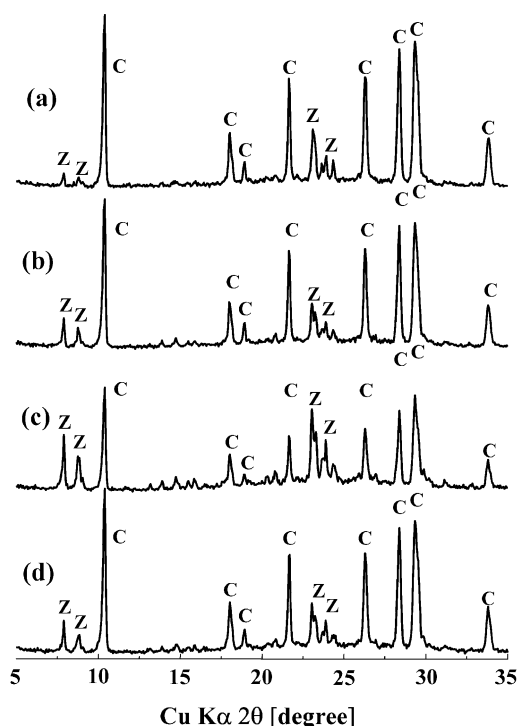


Fig. 4. XRD patterns of ZSM-5 zeolite coated samples; (a) sample coated a precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$  on as-received substrate, (b) sample coated a precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$  on 3 h leached substrate, (c) sample coated a precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$  on 6 h leached substrate, (d) sample coated a precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 700$  on 3 h leached substrate. Z: ZSM-5 zeolite and C: cordierite (substrate).

### 3.3. ZSM-5 zeolite coated sample

ZSM-5 films were formed on the as-received, 3- and 6-h leached honeycomb substrates produced from metakaolinite-derived microporous silica. Fig. 4 shows the XRD pattern of these samples. The XRD peak intensity of ZSM-5 increased with increased leaching time of the substrate, indicating that the silica-rich surface facilitates zeolite formation because the chemical composition of the substrate becomes  $\text{SiO}_2$ -rich after acid treatment (48.5 mass% in the as-received sample, 75.1 mass% in the 6-h leached sample). Fig. 5(a) shows a cross section of the honeycomb cell corner with its ZSM-5 film. The thickness

of the film is about 30–40  $\mu\text{m}$ , but was thicker in the corners. The inset shows the surface of the uniformly distributed zeolite layer. The number of macropores in the zeolites observed in these samples (Fig. 5(b)) were reduced by repeated crystallization. The ZSM-5 crystals in the film shown in Fig. 6(a) are prismatic and of uniform size ( $< 1 \mu\text{m}$ ), similar to the ZSM-5 powder synthesized from leached metakaolinite [10]. By contrast, microstructures of the films formed on highly leached substrates with a high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio showed well-crystallized and inter-grown ZSM-5 grains 3–5  $\mu\text{m}$  in size (Fig. 6(b)). This morphology is similar to alumina-free ZSM-5 (silicalite-1), indicating that a  $\text{SiO}_2$ -rich interface and high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio enhance crystallization of ZSM-5 zeolite from its metakaolinite precursor.

The porous properties of honeycomb substrates coated with ZSM-5 films are listed in Table 1. The increase in total SSA of the coated samples is not significant, especially for the leached substrates, because the  $\text{SiO}_2$ -rich layer formed after leaching had a high SSA. However, the internal SSA increased in all the samples after zeolite formation. A greater increase (about 1.5 times) was observed in samples with a high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and in highly leached samples. A similar trend observed in the micropore volume is attributed to the growth of microporous zeolite in the mesopores and macropores of the substrates and to the possibility of the  $\text{SiO}_2$ -rich interface converting to zeolite. The pore size distribution shows micropores of less than 1 nm and others of about 2 nm, attributed to intra and inter-crystal porosity, respectively. Mesopores 4 nm in size in the support were reduced after repeated crystallization. As observed by microstructure and XRD analysis, higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios and the presence of greater amounts of the  $\text{SiO}_2$ -rich interface facilitates the formation of zeolite with well crystallized morphology, resulting in a higher micropore volume and internal SSA.

The amount of  $\text{NH}_3$  adsorption was obtained from the  $\text{NH}_3$ -TPD spectra of the three ZSM-5 coated samples prepared from the precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ . All the  $\text{NH}_3$ -TPD spectra show distinct peaks at about 100  $^\circ\text{C}$  (the l-peak corresponding to physisorption of  $\text{NH}_3$ ) and small peaks at around 300–400  $^\circ\text{C}$  (the h-peaks corresponding to

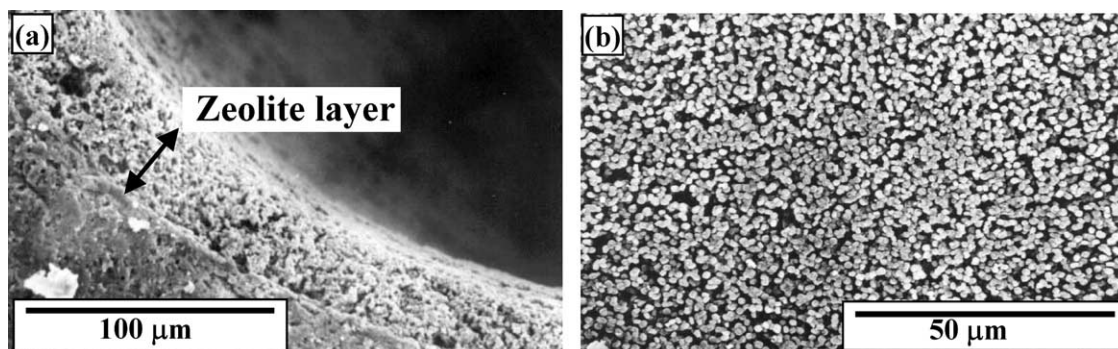


Fig. 5. SEM photographs of ZSM-5 film on cordierite substrate: (a) honeycomb cell corner with zeolite film, (b) surface of the ZSM-5 zeolite crystals.

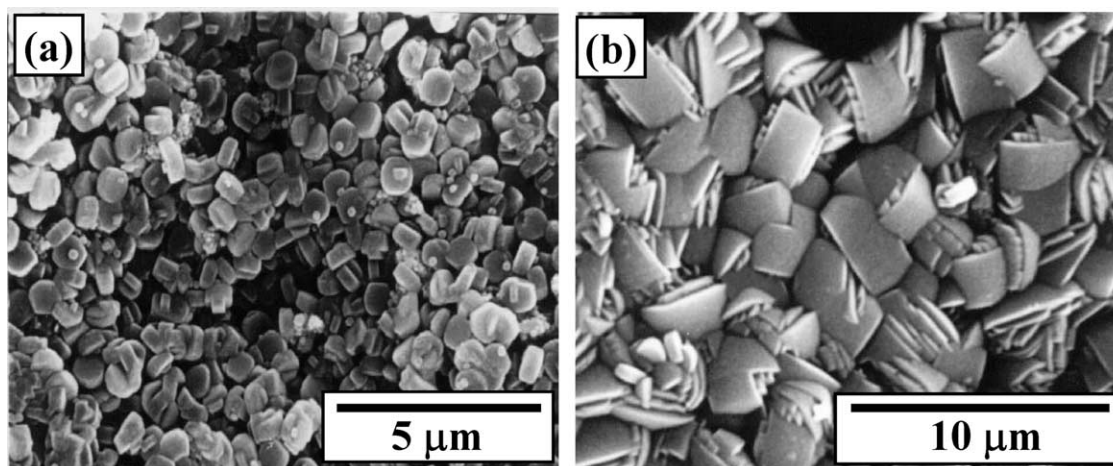


Fig. 6. SEM photographs of ZSM-5 crystals; (a) the crystals formed on 3 h leached substrate using the precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$ , (b) the crystals formed on 6 h leached substrate using the precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 700$ .

chemisorption of  $\text{NH}_3$  as a result of the solid acidity). The amounts of  $\text{NH}_3$  adsorption calculated from the areas of the l- and h-peaks are listed in Table 2. The amounts of physically adsorbed  $\text{NH}_3$  in the as-received, 3- and 6-h leached substrate samples are 0.39, 0.90 and 1.93 mmol/g, respectively. The large changes in the amounts of physisorption are related to the SSA values of the samples; the more highly leached sample containing more zeolite showed greater  $\text{NH}_3$  desorption in this temperature range. The amounts of physisorption calculated per unit SSA are thus similar in these three samples. By contrast, different behavior is observed in the peak areas and temperatures of the h-peaks of the three samples. The solid acidity of these

three samples therefore increases in the order as-received < 6 h leached < 3 h leached samples. Since the samples had different amounts of zeolite on their surfaces and showed different SSA values, the solid acidity was calculated per unit weight of ZSM-5 zeolite and also per unit of SSA. It becomes clear from these calculations that the solid acidity of the ZSM-5 zeolites formed on the three different types of cordierite honeycomb substrates is different even though the same precursor gel was used for the coating. The difference in the solid acidity can be attributed to changes in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the ZSM-5 zeolites, possibly due to the effect of the  $\text{SiO}_2$ -rich interfacial layer. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the ZSM-5 zeolite films measured by SEM-EDX

Table 1  
Porous properties of three types of cordierite honeycombs before and after coating with ZSM-5 zeolite from precursors with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios

Substrate	Precursor $\text{SiO}_2/\text{Al}_2\text{O}_3$	Total SSA ( $\text{m}^2/\text{g}$ )	Internal SSA ( $\text{m}^2/\text{g}$ )	External SSA ( $\text{m}^2/\text{g}$ )	Total pore volume (ml/g)	Micropore volume (ml/g)
As-received	–	1	–	–	0.01	–
	70	18	10	8	0.024	0.005
	100	42	25	17	0.040	0.010
Three-hour leached	–	81	33	48	0.055	0.019
	70	84	38	46	0.070	0.021
	100	110	58	52	0.110	0.030
	700	85	53	32	0.076	0.029
Six-hour leached	–	203	48	155	0.128	0.028
	70	203	89	114	0.143	0.049
	100	239	151	89	0.210	0.090

Table 2  
 $\text{NH}_3$  adsorptions of three ZSM-5 zeolite-coated cordierite honeycombs from a precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$

Substrate	l-Peak				h-Peak			
	Temp. ( $^{\circ}\text{C}$ )	Sample (mmol/g)	ZSM-5 (mmol/g)	$\mu\text{mol}/\text{m}^2$	Temp. ( $^{\circ}\text{C}$ )	Sample (mmol/g)	ZSM-5 (mmol/g)	$\mu\text{mol}/\text{m}^2$
As-received	100	0.39	3.9	9.2	300	0.14	1.44	3.4
3 h leached	100	0.90	5.3	8.1	410	0.31	1.81	2.8
6 h leached	100	1.93	8.8	8.1	315	0.21	0.96	0.9

Table 3  
Propane adsorption of three ZSM-5 zeolite-coated cordierite honeycombs from a precursor with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$

Substrate	Sample (mmol/g)	ZSM-5 (mmol/g)	$\mu\text{mol}/\text{m}^2$
As-received	0.009	0.086	0.20
Three-hour leached	0.015	0.085	0.13
Six-hour leached	0.003	0.014	0.01
ZSM-5	0.027	0.027	0.08

are 5.8, 11.6 and 46.9 in the as-received, 3- and 6-h leached substrates, respectively. Although these  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios appear to be influenced by lower values of the substrates, chemical reaction between the zeolite films and substrates is thought to lower the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the ZSM-5 zeolites below that of the precursor gel. Thus, the in situ crystallization method is expected to produce a strong adherence between the zeolite film and substrate.

The amounts of propane gas adsorbed by the ZSM-5 zeolite coated honeycombs are listed in Table 3, together with that of ZSM-5 powder as a reference. As shown in Table 1, the amount of zeolite coating increases with increasing substrate leaching time. By contrast, the amount of propane gas adsorption shows a different tendency with respect to the amount of zeolite, being highest in the 3-h leached sample. The amount of propane gas adsorbed on the sample leached for 3 h is smaller than that of the pure ZSM-5 powder reference sample but is much larger when calculated on the basis of the unit weight of ZSM-5 zeolite in the coated samples. This suggests that the ZSM-5 coated honeycomb samples prepared in this work have superior hydrocarbon adsorption properties, which is expected to be enhanced under flowing conditions because of the higher reactive surface area resulting from the loading of the ZSM-5 films on the honeycombs.

#### 4. Conclusion

Zeolite-A and ZSM-5 zeolite films were formed on three types of cordierite honeycomb substrates, i.e. as-received, 3- and 6-h leached, by an in situ crystallization method under soft hydrothermal conditions. The precursors, meta-kaolinite and microporous silica prepared by acid treatment of metakaolinite, were effective for the preparation of zeolite-A and ZSM-5 zeolite films as precursor gels prepared from alkoxides. Microporous silica is a very useful precursor for various types of zeolite because of its very wide  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, ranging from 2 to 1000. In the film formation, a re-coating method was effective in increasing the film thickness. The ZSM-5 zeolite films formed on the substrates can change their chemical composition and adsorption characteristics by the chemical composition and porous properties of the substrates through reaction in the interface of film and substrate. Increasingly vigorous acid leaching treatment of the cordierite substrates

increases the specific surface area and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the formed zeolite, resulting in increased ZSM-5 zeolite formation but decreased solid acidity and adsorption of propane gas. These results indicate that the in situ crystallization method is very effective for improving the adherence of the zeolite film to the substrate without degrading the mechanical strength of the substrate.

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