

In-Situ Crystallization of Zeolite Films on Ceramic Honeycomb Substrates from Metakaolinite Precursors

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Abstract- Zeolite A and ZSM-5 thin films were prepared on cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb substrates by in-situ crystallization using a kaolinite clay precursor. The zeolite films synthesized under hydrothermal conditions using both conventional heating and microwave heating were characterized by XRD, FTIR, SEM and N_2 adsorption. Zeolite A films formed by hydrothermal treatment of metakaolinite in alkaline solution at 80°C required 10 h of conventional heating but only 20 min of microwave heating. ZSM-5 films were formed on honeycomb substrates by hydrothermal treatment of microporous silica obtained by selective leaching of metakaolinite with TPA as the templating agent. The SiO_2/Al_2O_3 ratio and surface treatment of the substrates influenced the microstructure and porous properties of the resultant zeolite films. High SiO_2/Al_2O_3 ratios in the precursors and the presence of a silica-rich interface on the substrates resulted in well-crystallized zeolites with dense coatings and higher micropore surface areas.

Key words: Zeolite films, metakaolinite, in-situ crystallization, cordierite honeycomb substrates, microwave heating.

1. INTRODUCTION

Microporous zeolite films formed as a thin coating on inorganic supports have several advantages over bulk zeolites, with applications as adsorbents, catalysts, membranes and sensors. Zeolite films without any binder have been prepared on various substrates by in-situ crystallization on the substrate. Preparation methods for zeolite thin films and membranes are reviewed by Mizukami [1]. Zeolite A and ZSM-5 zeolites have been studied extensively because of their significant commercial applications. Zeolite films coated on multi channel honeycomb monoliths have the advantage of high geometric surface area resulting in a more active zeolite surface and a large open frontal area giving very little resistance to flow. They find applications as hydrocarbon adsorbents and deNO_x catalysts in automotive exhaust systems, highly permeable membranes for gas separation, etc. Zeolite films on cordierite honeycomb substrates have been prepared by conventional hydrothermal methods [2,3] and by modified in-situ crystallization methods [4,5].

Zeolites are generally synthesized under hydrothermal conditions, crystallizing from a solution containing SiO_2 , Al_2O_3 and Na_2O sources with optional templates or seeds. Various raw materials have been used for synthesizing ZSM-5 and other high silica zeolites [6]. Clay, being a hydrated aluminosilicate, is an important natural raw material for zeolites. Of the various clays, kaolinite ($Al_2Si_2O_5(OH)_4$) has a SiO_2/Al_2O_3 ratio of approximately 2, making it suitable for preparation of the zeolite A. It is thus used for zeolite A manufacture [7,8]. It is also used for the preparation of other low silica zeolites such as X, Y [9,10] and ZSM-5 with additional silica [11]. The preparation of microporous silica with a high surface area by selective

leaching of metakaolin has been reported [12]. This powder has been used as a cost-effective starting material for preparing ZSM-5 with SiO_2/Al_2O_3 ratios up to 700 [13].

Synthesis of zeolites A, X and ZSM-5 by microwave heating (MH) has shown advantages over conventional heating (CH) such as faster crystallization, smaller crystal size with high surface area and activity and avoidance of undesirable phases [14,15]. Some work has been done on preparation of zeolite film by MH. Most of the work reported on zeolite membrane formation by MH is concern the preparation of $AlPO_4$ [16] and zeolite Na A [17,18] on alumina supports.

The objective of the present work is to use metakaolinite as a precursor for hydrothermal synthesis of zeolite A and ZSM-5 films on cordierite honeycomb substrates by in-situ crystallization using CH and MH methods.

2. EXPERIMENTAL

The substrates used were cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb monoliths with a cell density of 400 cells per square inch (CPSI) 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 to 5 μm in size. Samples of 1x1x1 cm^3 were cut from the honeycomb monolith and used as substrates. Some of these samples were leached with 10 mass % sulfuric acid at 70 °C for 0 to 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.

2.1. Zeolite A film synthesis

Kaolinite (Georgia, USA), calcined at 800 °C for 4 h was mixed with NaOH and water for 12 h to produce a molar composition of $Al_2O_3:SiO_2:Na_2O:H_2O$: 1:2:4:100.

The substrates were dipped in the mixture and aged overnight. Both the solution and substrate was heated in a Teflon lined autoclave placed in an electric oven at 80 °C for 6 to 10 h.

2.2. ZSM-5 film synthesis

Microporous silica was prepared by selective leaching from metakaolinite, calcined at 600 °C for 24 h [12]. The calcined clay was treated with 20 mass % sulfuric acid (2.5 M) at 90 °C for 2 and 6 h with stirring, washed with dilute H₂SO₄ (0.5 M) and three times with deionized water before filtering. The microporous silica thus obtained had SiO₂/Al₂O₃ ratios of 70 and 700. The zeolite precursor was prepared by mixing these microporous silica powders with water, tetrapropylammonium hydroxide (10% TPAOH, Wako Chemicals, Japan) and NaOH in the molar ratio SiO₂: TPAOH : NaOH : H₂O = 100 : 10 : 10 : 2000. 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 surface solution removed by careful air blowing. The samples were heated in a Teflon lined autoclave with a small amount of water at 150 °C for 24 h.

2.3. Microwave heating (MH)

For MH synthesis, a microwave oven (2.45 Hz, 800W) was used rather than a conventional oven. The substrates were heated with zeolite precursor solution in a sealed Teflon vessel for 5 to 60 minutes.

After the hydrothermal treatment, 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.

2.4. Characterization and testing

The formation of zeolite film on as prepared samples was confirmed by powder X-ray diffraction (XRD; RIX 2000 Rigaku, Japan). The Fourier transformed infrared (FTIR) spectra were measured by the KBr method using an FTIR spectrometer (FTIR 8200PC, Shimadzu, Japan). The porous properties were determined from N₂ gas adsorption and desorption isotherms measured at 77K using an Autosorb-I instrument (Quantachrome, USA). The specific surface area (SSA) was calculated by the BET method, the pore size distribution (PSD) was calculated by the BJH method and the pore volume was obtained from the maximum adsorption at a relative pressure of 0.999. The micropore volume and micropore surface areas were calculated using the t-plot method. The microstructure of the zeolite film on the honeycomb substrate was observed using a scanning electron microscope (SEM; S-2050, Hitachi, Japan).

3. RESULTS AND DISCUSSION

3.1. Synthesis of Zeolite A film

Zeolite A film was formed by CH at 80 °C for 10 h. Fig. 1 shows the XRD patterns of zeolite A films on cordierite honeycombs formed by CH at 80 °C for 10 h. The peak intensities of zeolite A increased after repeated coating (b) because of greater coverage and increased zeolite film formation. Fig. 2 shows the XRD patterns of zeolite A films on cordierite substrates prepared by MH for 5 to 30 min. Formation of zeolite A was detected after 10 min of reaction. Improving after 20 min, but unhydrated aluminosilicate started forming after 30 min

due to overheating. The product phase changed completely to unhydrated aluminosilicate after 40 min. This was also confirmed by the XRD of powders obtained from the synthesis solution, which showed a halo after 5 min, zeolite A after 10 to 30 min. and unhydrated aluminosilicate after 40 min. The amount of zeolite A formed after re-coating by MH for 20 min is about 19 mass %, similar to the result from the CH method. FTIR spectra showed absorption bands at 466, 554, 664 and 1000 cm⁻¹, in agreement with zeolite 4A [7].

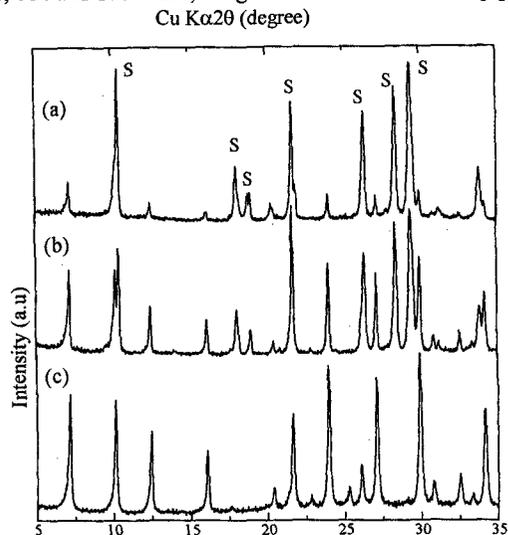


Fig 1. (a) XRD of zeolite A film on cordierite (marked as S) substrate by CH, (b) after re-coating and (c) zeolite A powder sample.

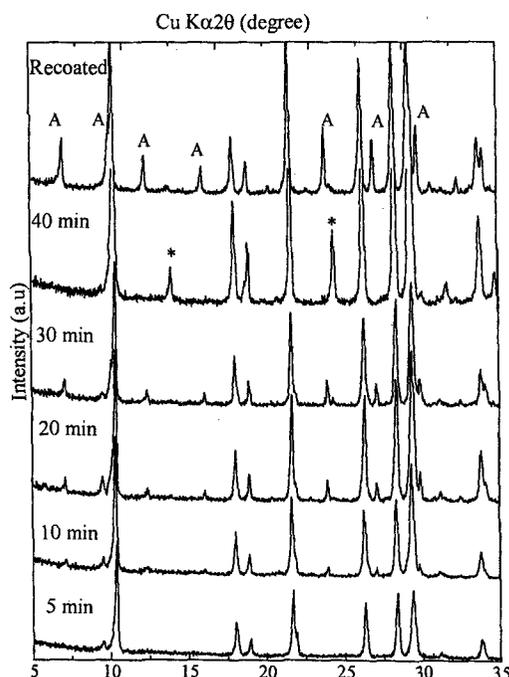


Fig 2. XRD patterns of Zeolite A (marked as A) film on cordierite substrates prepared by MH for different times. Impurity phases are shown as *

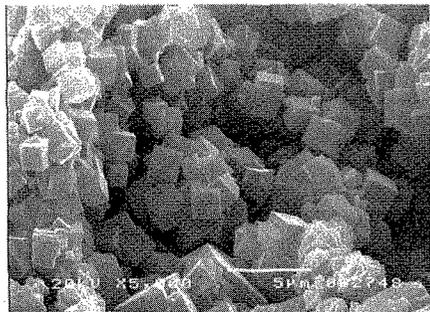


Fig 3. SEM photographs of zeolite A film on cordierite substrates.

The microstructure of zeolite film formed on a substrate by CH is shown in Fig.3. A zeolite film layer about 15 to 30 μm thick was observed on the honeycomb cells. The zeolite A crystals composing the film were cubic in shape with uniform sizes of about 3 μm . Pores between the crystals and aggregates resulted in discontinuity of the film, due to a rough surface and the presence of non-uniform macro pores on the surface of honeycomb substrate. Repeated in-situ crystallization not only improved the film continuity but also increased its thickness. The microstructure of zeolite A film prepared by MH does not reveal any distinct differences, justifying the usefulness of this alternative method.

The mechanism of zeolite film formation can be considered in terms of the following steps; dissolution of the distorted metakaolinite structure in alkali, saturation of the pores and surfaces of the porous substrate and crystallization on the substrate. The kinetics of zeolite formation depend on the crystallinity of the clay, its calcination temperature, the concentration of alkali, the reaction temperature and time [10]. When the first three parameters were kept identical as in the present experiments, MH drastically reduced the dissolution and crystallization times, resulting faster formation of zeolite A film compared to CH. This mechanism of zeolite A film formation is a result of combined thermal and microwave effects [18].

3.2. Synthesis of ZSM-5 film:

ZSM-5 film was formed on unleached, 3 h leached and 6h leached honeycomb substrates using metakaolinite - derived microporous silica as the starting material. Fig. 4 shows the XRD pattern of these samples. The peak intensity of ZSM-5 increased with increased leaching time of the substrate indicating that the silica rich surface facilitated the zeolite formation. Fig.5a shows a cross section of the honeycomb cell corner with its ZSM-5 film. The thickness of the film was about 30 to 40 μm , but was more thicker in the corners. The inset shows the surface of the zeolite layer uniformly distributed. Macro pores between zeolites were also observed in these samples but were reduced by repeated crystallization. The ZSM-5 crystals in the film shown in Fig 5 b, are plate-like and of uniform size (about 2 μm), similar to ZSM-5 powder synthesized from leached metakaolinite [13]. 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 to 5 μm in size (Fig.5c). This morphology is similar to alumina-free ZSM-5 (silicalite-1), indicating that a silica - rich interface and high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio enhances

crystallization from metakaolinite precursor. It is expected that these layer will have a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (>700) than the precursor.

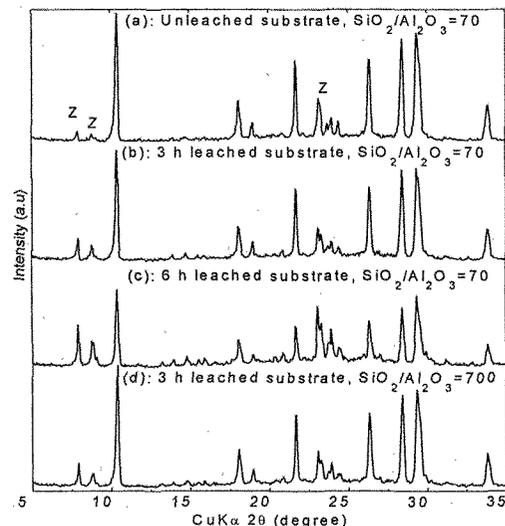


Fig 4. XRD of ZSM-5 (marked as Z) films on cordierite substrates prepared by CH.

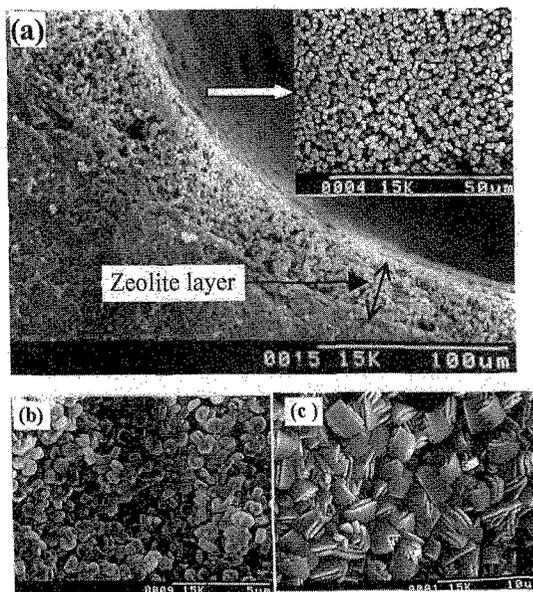


Fig 5. SEM photographs of ZSM-5 film on cordierite substrate formed by CH; (a) honeycomb cell corner with zeolite film. (b) ZSM-5 crystals in the film on 3h leached substrate for $\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$. (c) ZSM-5 crystals in the film on 6h leached substrate for $\text{SiO}_2/\text{Al}_2\text{O}_3 = 700$.

The porous properties of honeycomb substrates coated with ZSM-5 films are shown in Table 1. The increase in total specific surface area (SSA) is not significant in the coated samples, especially on the leached substrates, because the silica 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 with a high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and highly leached samples. A similar trend was also observed in the micropore volume. This is attributed to the growth of microporous zeolite in

Table I. Porous properties of cordierite honeycomb substrates with ZSM-5 film before and after coating.

SiO ₂ /Al ₂ O ₃ ratio	Substrate treatment	ZSM-5 coating	Micro pore volume (ml/g)	Total pore volume (ml/g)	Int SSA (m ² /g)	Ext SSA (m ² /g)	Total SSA (m ² /g)
70	Unleached	Before	-	-	-	-	1
70	Unleached	After	0.005	0.024	10	8	18
70	3 h leached	Before	0.019	0.055	33	48	81
70	3 h leached	After	0.021	0.070	38	45	84
70	6 h leached	Before	0.028	0.128	48	155	203
70	6 h leached	After	0.049	0.143	89	114	203
700	3 h leached	Before	0.019	0.055	33	48	81
700	3 h leached	After	0.029	0.076	53	32	85

* Int SSA : Internal specific surface area

Ext.SSA : External specific surface area.

the mesopores and macropores of the substrates. The pore size distribution showed 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 SiO₂/Al₂O₃ ratio and higher silica-rich interface facilitates zeolite formation with well crystallized morphology, resulting in a higher micropore volume and internal SSA.

An attempt was made to prepare ZSM-5 films on honeycomb substrates using a domestic Microwave (MW) oven, based on the observation that ZSM-5 crystallization is faster in the metakaolinite precursor [13]. Zeolite films were not formed even after heating for 1 hr. MH preparation of ZSM-5 film requires special fixtures allowing a high-pressure autoclave to be placed in the microwave cavity which must also have an IR based temperature sensor to maintain the temperature. It is very difficult to prepare ZSM-5 in a domestic MW oven because of the difficulty to obtain and maintain a high temperature (150-175 °C). Over-heating will cause the template ions to degrade. Most of the reported MH syntheses used a special MW autoclave. In a novel approach, MH using a domestic MW oven was employed as a complementary heat treatment to CH to achieve faster crystallization of zeolite. A ZSM-5 film was formed after 20 min of MH followed by 12 h of CH at 150°C. The properties obtained are similar to CH of 24 h at 150°C. This faster crystallization is assumed to be due to the initiation of zeolite nucleation during MH, with further crystallization occurring during CH. Detailed studies are being carried out to optimize this method and to understand the mechanism.

4. CONCLUSIONS

Naturally available clay (kaolin) was effectively used as a cost-effective precursor for crystallizing zeolite A and ZSM-5 thin films on ceramic honeycomb substrates by a soft solution approach. The zeolite A film was formed by both conventional heating and microwave heating of substrates in the alkaline solution. ZSM-5 films were formed from a precursor containing micro porous silica obtained from selective leaching of metakaolinite, together with template ions. The SiO₂/Al₂O₃ ratio and surface treatment of the substrates was found to influence both ZSM-5 film formation and its porous properties.

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