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Microwave-assisted hydrothermal synthesis of zeolite films on ceramic supports

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Zeolite films were formed on ceramic supports by a novel microwave-assisted hydrothermal method and were characterized by XRD, SEM, FTIR and BET surface area. The two-stage synthesis technique consists of microwave heating of supports saturated with precursor solution to form a thin layer of zeolite nano-seeds, followed by hydrothermal treatment to crystallize MFI zeolite. The resulting zeolite formation time was drastically reduced and the BET surface area of the product was double that obtained using conventional hydrothermal method. The dipping time, microwave heating time, power and hydrothermal heating time influence the amount of zeolite formation, the BET surface area and preferred orientation of the zeolite film. This new method of seed-film growth using a simple domestic microwave oven has the advantages of a two-stage synthesis technique, allowing independent control of nucleation and crystallization to obtain an optimum zeolite film and reduce the synthesis time.

1. Introduction

Zeolite films prepared on inorganic supports have several advantages over bulk zeolites and hence are used for applications such as adsorbents, catalysts, membranes and sensors [1, 2]. Much work has been done on zeolite films with MFI structures such as silicalite-1 and ZSM-5 because of their wide range of applications, for selective gas separation, hydrocarbon adsorption, DeNOx catalysts, etc. The preparation of zeolite films by *in-situ* crystallization on supports under hydrothermal conditions results in a strong interface due to chemical bonding and hence many methods including wet hydrothermal, dry gel conversion, etc. have been developed [3]. One recently-reported method, the seed film method, gives flexibility to control nucleation, seeding and growth, and by controlling the seed size and density, the orientation of the final film can be varied. This method involves the initial adsorption on the surface of the substrate of zeolite seeds, which are subsequently grown to zeolite crystals by hydrothermal treatment [4].

The ceramic supports commonly used are alumina (α-Al_2O_3) disks or tubes but multi-channeled monolithic honeycomb substrates have the advantages of higher geometric surface area and low back-pressure. Zeolite films on cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb substrates have been prepared by conventional hydrothermal methods for DeNOx applications [5]. *In-situ* crystallization in the presence of water vapor has been used to avoid the prolonged dipping of substrates in alkaline solution [6]. Boron-ZSM-5 membranes have been prepared on alumina-coated SiC honeycomb monoliths by *in-situ* hydrothermal synthesis [7]. All these preparation methods involve hydrothermal treatment for 24 to 72 h, but the formation of a uniform zeolite film on the macro porous honeycomb support is still difficult to achieve.

Synthesis of zeolites A, X, Y and ZSM-5 by microwave heating (MH) has the advantages over conventional heating (CH) of promoting faster crystallization, smaller crystal size and the avoidance of undesirable phases by shortening the synthesis time [8–12]. Some work has been reported on the preparation of zeolite film and membranes by MH, most of which was on $AlPO_4$ [13] and zeolite A [14, 15] using alumina supports. The MH preparation

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of ZSM-5 requires a special microwave digestion system in which a high-pressure autoclave is located in the microwave cavity with a pressure controller and optical temperature sensor to maintain the temperature. It is very difficult to prepare ZSM-5 in a domestic microwave oven because of the difficulty of achieving and maintaining the necessary high temperatures (150–175°C). Over-heating will cause the templates to degrade.

A new method for preparing MFI zeolite films using a simple domestic microwave oven was developed using a two-stage synthesis approach. Microwave heating (MH) is used to form a thin layer containing nano particles of zeolite seeds, which act as nucleation sites. Hydrothermal treatment is then used to grow MFI crystals on these nuclei. The main advantages of this method are that the preparation of the zeolite films on honeycomb monoliths is of short duration and produces a good surface coverage. We refer to this method as microwave-assisted *in-situ* crystallization (MAIC). This method is described here and the effect of microwave heating time, power, hydrothermal heating time, etc is discussed in relation to the mechanism of zeolite film formation.

2. Experimental procedure

2.1. Preparation of zeolite film

The ceramic supports were cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb substrates and alumina (α-Al_2O_3) disks. The cordierite honeycomb substrate (BHEL, Bangalore, India) had a cell density of 400 cells per square inch (cpsi), a wall thickness of 0.17 mm and a porosity of 35%. The alumina disks were of 20 mm dia and 2 mm thickness with varying porosity (0 to 50%). The zeolite precursor solution was prepared from colloidal silica (30%, Nissan Chemicals, Japan) and tetrapropylammonium hydroxide, (TPAOH, Wako Pure Chemicals, Japan). A precursor solution with a molar ratio of SiO_2:TPAOH:H_2O = 100:10:1800 was prepared by stirring for 3 h at room temperature. The substrate samples were dipped in the precursor solution for 2 h, removed from the solution and the excess on the surface removed by careful air blowing.

The zeolite film synthesis was carried out in two stages, consisting of microwave heating (MH) and hydrothermal treatment (HT). In the MH stage, the honeycomb substrate samples saturated with zeolite precursor were placed in a sealed Teflon vessel and heated in a domestic microwave oven (2.45 GHz, 800 W) for 2 to 15 min. Full power was used in most of the experiments but a few trials with 25 and 50% power were also carried out. For the hydrothermal treatment, the microwave-heated samples were placed in a Teflon lined autoclave, which was filled with the precursor solution to cover the substrates (60 to 70% volume of the container) and heated in a conventional oven at 150°C for 3 to 24 h. After autoclaving, the samples were washed with distilled water in an ultrasonic bath for 10 min to remove any loosely-bound coating, especially in the corners of the honeycomb. After drying at 110°C for 1 day, the samples were calcined at 600°C for 2 h to remove the template ions. The calcined samples were again washed with distilled water in an ultrasonic bath for 10 min to remove any thick coating detached during calcination. For comparison, the zeolite films on honeycomb substrates were also prepared by a conventional hydrothermal method under similar conditions. These samples are designated as CH whereas the samples prepared by the two-stage, microwave assisted *in-situ* crystallization method are referred to as MAIC.

2.2. Characterization and testing

The formation of zeolite was confirmed by X-ray diffraction (XRD; Geigerflex, 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 of the supported zeolite film were determined by the BET method from N_2 gas adsorption and desorption isotherms measured at 77 K using an Autosorb-I instrument (Quantachrome, USA). The microstructure of the supported zeolite film was observed using a scanning electron microscope (SEM, S-2050, Hitachi, Japan).

3. Results and discussion

3.1. Formation of ZSM-5: effect of hydrothermal treatment time

The XRD patterns of ZSM-5 (MFI structure) films on cordierite honeycomb substrates formed at 150 °C by MAIC at various hydrothermal treatment times are shown in Fig. 1. ZSM-5 peaks were clearly observed after 4.5 h and complete coverage by the zeolite film occurred after 6 h. The cordierite peak intensity gradually decreased with increasing hydrothermal treatment time, practically disappearing after 6 h in the MAIC sample and after 24 h in the CH sample. This reflects the increasing amounts of zeolite gradually forming on the cordierite surface; the formation rate of zeolite in the MAIC sample is being much faster than in the CH sample. The formation of zeolite in the 12 h MAIC sample is thus equivalent to that formed after 24 h of CH sample. The amount of zeolite formed in the MAIC samples as determined by weight-change measurements was 3% after 3 h, 11% after 4.5 h, 18% after 6 h, 22% after 12 h and 30% after 24 h. This is about two times larger than that in the CH samples. The XRD peaks indicate a preferred orientation to (020), which is the large face in the MFI crystals composing the film. Maximum orientation was observed in the MAIC samples after 12 h, but this preferred orientation decreases in the 24 h sample in which the film is thicker.

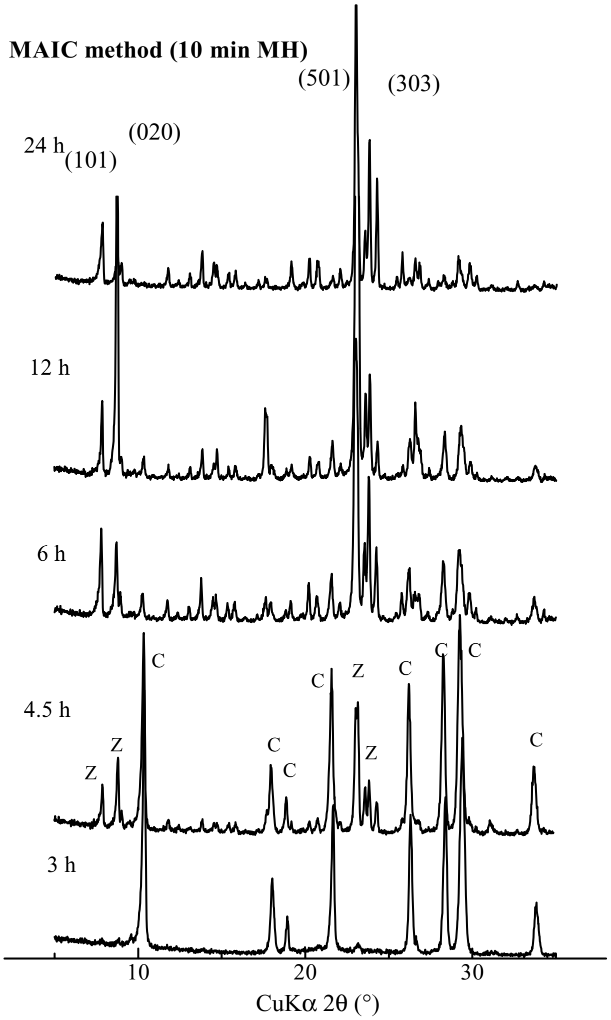

Figure 1 XRD patterns of MFI film on cordierite honeycomb supports formed at various hydrothermal treatment times at 150°C by the MAIC method. Z: ZSM-5 and C: Cordierite.

Fig. 2 shows the SEM of the zeolite film formed on a honeycomb substrate. Well- crystallized MFI crystals (10 × 20 micron) with typical hexagonal prismatic morphology completely cover the substrate. The platy crystals are predominately oriented with their larger face on the surface, as shown in Fig. 2a for the 6 h treated sample. Fig. 2b shows the sample cross-section with the zeolite crystals forming on a corner of the honeycomb substrate. A very uniform film of about 60–75 micron thickness was obtained, increasing to about 75 to 100 microns at the corners of the honeycombs due to the greater attachment of zeolite crystals in that area. The FTIR spectra of the MAIC samples show characteristic absorption bands at 450 & 550 cm^{-1} assigned to MFI.

Comparison of the kinetics of zeolite formation and the amount of zeolite formed in the CH and MAIC method is best understood in terms of the BET surface area data. Fig. 3 shows the change in BET specific surface area (SSA) of the samples prepared at different hydrothermal

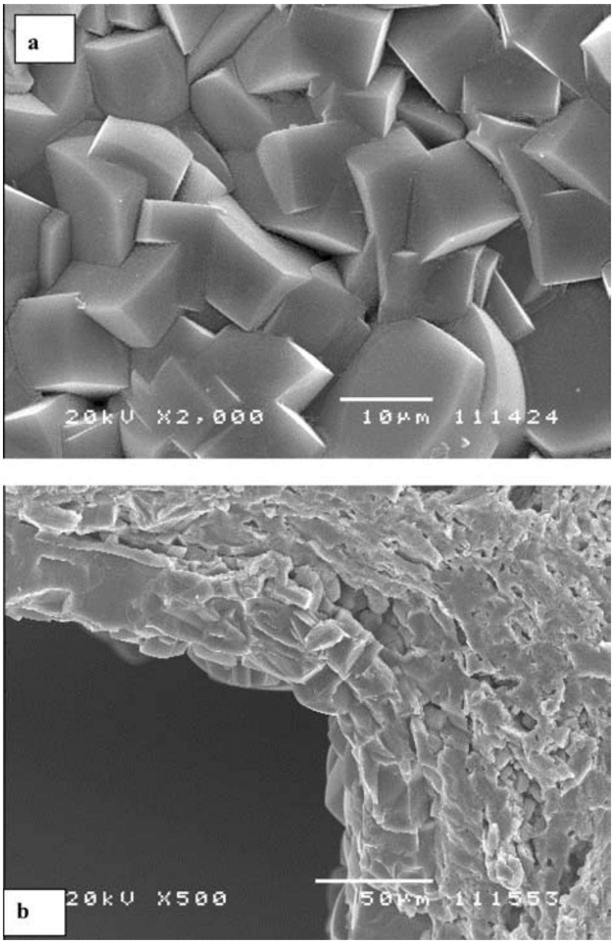

Figure 2 SEM photographs of zeolite film on a honeycomb support prepared by MAIC with a hydrothermal treatment time of 6 h (a) and cross-section of the honeycomb corner (b).

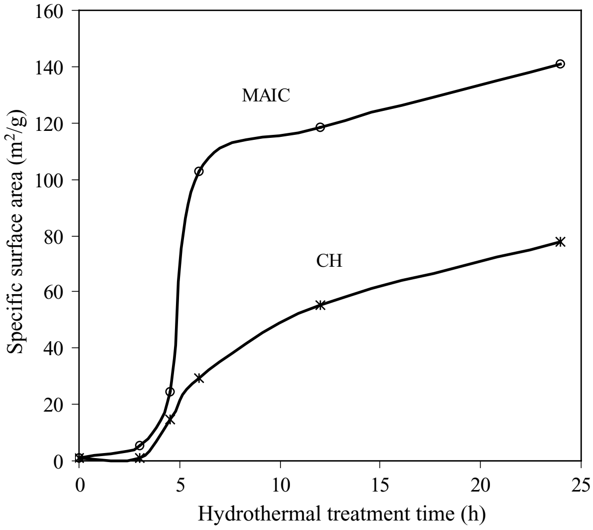

Figure 3 BET specific surface areas of cordierite honeycomb substrates containing a zeolite film prepared at various hydrothermal treatment times by MAIC and CH methods.

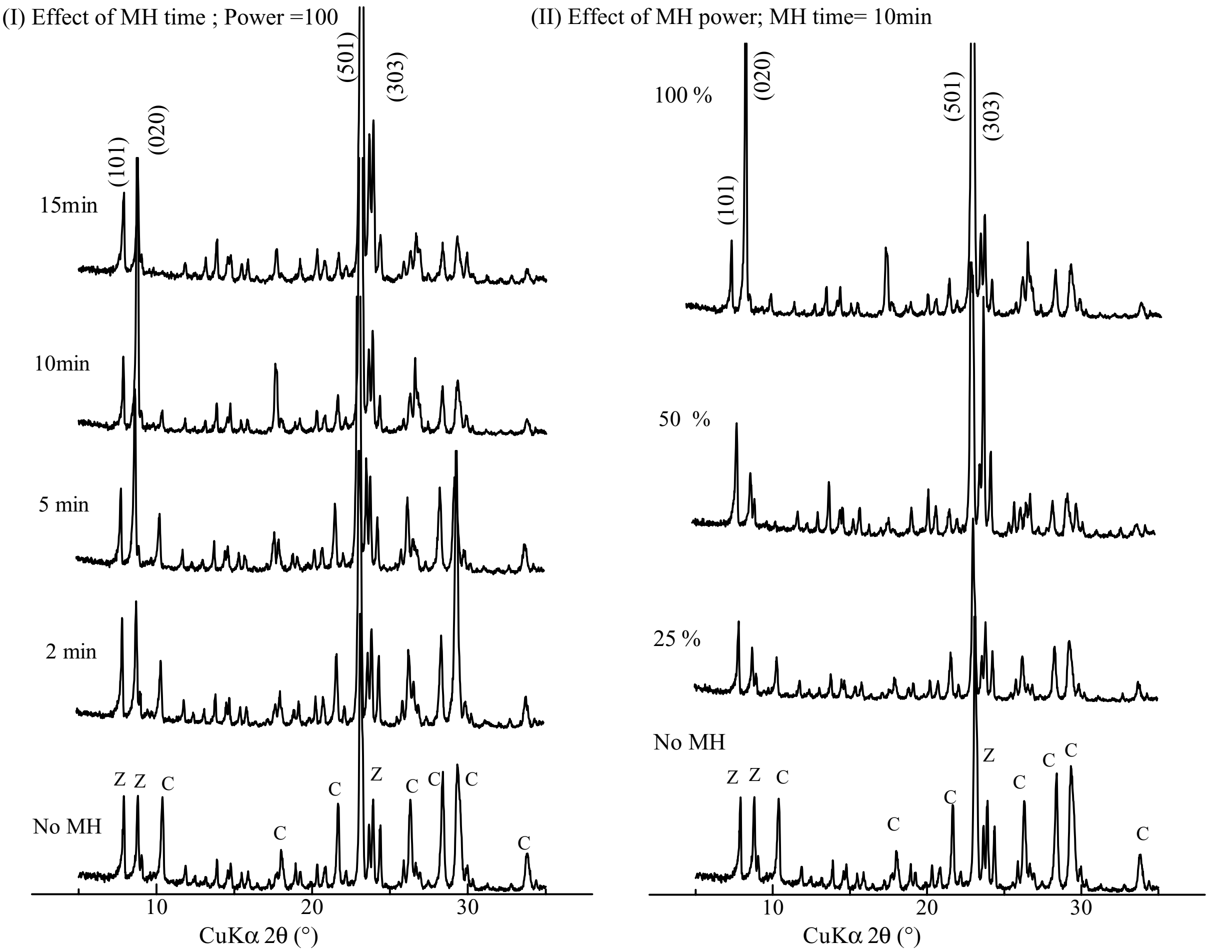

Figure 4 XRD patterns of MFI films on cordierite honeycomb formed by microwave heating and hydrothermal treatment at 150°C for 12 h; (I) Effect of MH time and (II) Effect of MH power.

treatment times for MAIC and CH samples. The MAIC samples show SSA values which are more than double those of the SSA of the CH samples. The SSA increases sharply in MAIC after 6 h reaction because of very good coverage by the zeolite film. There is a subsequent small increase in the SSA value from 6 to 24 h. The SSA of the 24 h MAIC sample was 141 m^2/g. In the CH samples, the SSA shows only a gradual increase up to 24 h and even after 24 h the SSA is only 77 m^2/g. The higher SSA values of the MAIC samples are attributed to the larger amount of zeolite film and the formation of well crystallized zeolite on the surface of the porous substrate. By contrast, complete coverage by the zeolite was very difficult to achieve in the CH samples. The pore size distributions of the samples (MAIC) prepared by hydrothermal treatment $>$ 6 h show only micropores and no mesopores. However, CH samples treated up to 12 h show some meso and macro pores.

3.2. Effect of MH time and power

The effect of microwave heating time and power during MH was analyzed by comparing all the samples which are hydrothermally treated at 150°C for 12 h. Fig. 4(i) shows the XRD peaks of the samples prepared by MH for various times at 100% power and then hydrothermally treated at 150°C for 12 h. The ZSM-5 peak intensity increases with increasing MH time, complete coverage being observed after 15 min. An increase in the preferred orientation of (020) peak is observed with increasing MH time up to 10 min but orientation decreased at 15 min. This indicates that the growth of the (020) oriented film increases with MH time, reaching a maximum at 10 min but the orientation decreases after 15 min due to the formation of a thicker zeolite film. Thus, an MH time of 10 min was used in all further experiments. The MH power also influences the peak intensity and orientation of the zeolite (Fig. 4(ii)). The ZSM-5 peaks show less orientation at 25 and 50% power but a greater degree of preferred orientation at 100%.

Changes in the SSA with MH time and power are shown in Fig. 5. The effect of MH treatment on the SSA is not significant up to 2 min. Above 2 min, the SSA increases with increasing MH time. This may mean that 2 min is necessary to reach the maximum temperature of the microwave

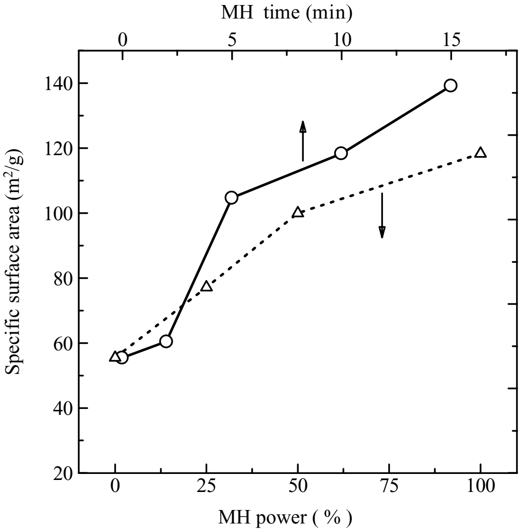

Figure 5 Effect of MH time and power on the BET specific surface area of samples prepared under hydrothermal treatment of 150°C for 12 h.

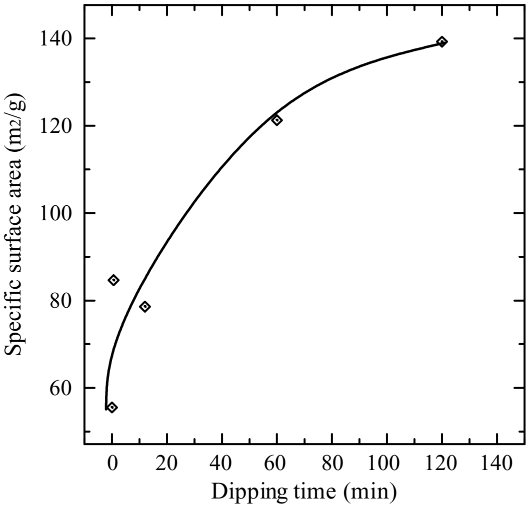

Figure 6 BET specific surface area of cordierite honeycomb substrates containing zeolite film prepared using various dipping times before microwave heating.

oven. After microwave heating for > 5 min the formation of nuclei begins, producing more zeolite crystals with increasing MH times. The SSA also increases linearly with MH power up to 50% but less steeply above 50% power. The higher MH power produces a higher temperature, resulting in the formation of larger zeolite crystals. The temperature at 25, 50 and 100% power was measured indirectly as 80–85, 95–100, 100–110°C, respectively. Higher nucleation temperatures produced larger nuclei in smaller numbers resulting in larger zeolite crystals. This is the reason for a greater degree of zeolite formation and greater preferred orientation at the maximum MH power. By contrast, increasing the MH time results in the formation of more nuclei and thus the resulting zeolite film consists of smaller, densely packed crystals. Thus, it should be possible to control the morphology of the zeolite film on the support by controlling the MH time and power in MAIC method, as with the seed-film method [4].

3.3. Effect of dipping time

Most of the above experiments were conducted by completely saturating the porous honeycomb supports with the precursor before MH treatment. This was done by dipping the support for 2 h, so that the maximum filling of the pores will result in the formation of the maximum number of zeolite nuclei and the greatest amount of zeolite film. Thus, a thick film was obtained (of the order of 75 to 100 microns) which is good for applications other than separation. For the formation of membranes, the film should be thin, ideally limited only by the cell dimensions of zeolite. When macroporous supports are used, the zeolite also forms in the pores, reducing the flux. To avoid this, either the formation of a mesoporous intermediate film [7] or the use of masking methods [16] is required. The effect of dipping time was studied to determine the possibility of controlling zeolite formation inside the pores. Honeycomb substrates were dipped in the precursor solution for 36 sec, 12 min, 1 h and 2 h and microwave heated for 10 min followed by hydrothermal treatment at 150°C for 12 h. Fig. 6 shows the effect of dipping time on SSA. A dipping time of 0 refers to the samples without MH treatment (CH method). The SSA increases when the dipping time increases from 0 to 36 sec, indicating that the smallest numbers of zeolite nuclei enhance zeolite formation. Little difference was found between samples dipped for 36 sec and 12 min, but the SSA increases in the 1h-dipped sample because a greater amount of precursor fills the pores. Dipping for 2 h further increased the SSA, but to a lesser extent, suggesting that saturation of all the pores with precursor has occurred by 2 h. This thickness control is only possible with MAIC but not with CH unless a masking technique is used [16]. In the MAIC method, the layer containing the zeolite nuclei, which forms on the surface of pores acts as a barrier, preventing the filling of the pores by the precursor and resulting in zeolite crystallization predominately on the surface of the substrate. The present experiments give an the indication of this mechanism, which could be explored further by detailed permeation experiments.

3.4. Zeolite film synthesis on alumina disks

The synthesis of ZSM-5 zeolite on α-alumina disks of varying porosity (0, 20, 40 and 50%) was successfully carried out and was confirmed by XRD. Zeolite films were formed by both MAIC (with a microwave heating time of 15 min and hydrothermal heating time of 12 h) and CH methods. The amount of zeolite formed and the XRD intensity was measured, and compared to find out

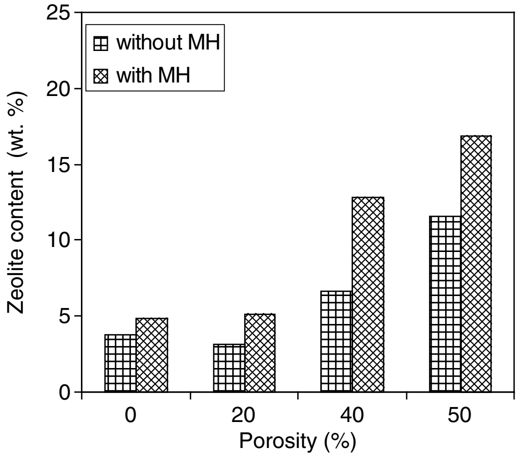

Figure 7 Effect of porosity on the amount of zeolite formed on alumina supports by the CH and MAIC methods.

the effect of porosity. Fig. 7 shows the amount of zeolite formed by MAIC and CH on alumina substrates of varying porosity. The amount of zeolite formed increased with porosity for both CH and MAIC. The increase due to the influence of MH is 1.3 times for zero porosity and 1.5 times for 50% porosity. The XRD peak intensity ratios also show this trend. Essentially the same degree of increase was obtained at all porosity levels, indicating that the microwave effect is predominates over the porosity effect.

3.5. Mechanism of film formation

The faster and extensive formation of zeolite films on porous supports by the MAIC method is suggested to arise from the following mechanisms: (1) Saturation of the pores with higher concentration of zeolite precursor during MH increases the quantity of zeolite formed after hydrothermal treatment. This depends on the substrate porosity and dipping time. (2) The formation of nuclei or nano-sized seeds during MH which facilitates the fast formation of zeolite. This depends on the MH time and power. These nano-sized nuclei fill the pores of the substrate and provide nucleation sites or seeds. Thus, the MH step can be considered as the nucleation stage. In the second stage (hydrothermal treatment), the nuclei grow to form MFI crystals and hence this is the crystallization stage. During this stage, fresh nuclei are also formed throughout the solution but mainly on the substrate, increasing the film thickness. Nucleation is a continuous process, but if it is completed in the MH stage (e.g. with 10 min heating at 100% power), the second stage is dominated by crystallization, similar to that reported for two-stage silicalite-1 synthesis [4]. In the conventional method, both nucleation and crystallization take place during hydrothermal treatment, thus requiring more time to form well-crystallized zeolite films

The present experiments indicate that though the filling of pores with more zeolite precursor has a beneficial effect on the amount of zeolite formation, microwave heating significantly influences the formation of nuclei on the support and enhances the crystallization rate in the two-stage synthesis method described here. This technique, using a simple domestic microwave oven, has the advantages of a two-stage synthesis technique for independently controlling the nucleation and crystallization to obtain an optimum zeolite film and shorten the synthesis time.

4. Summary

This paper describes a two-stage synthesis technique, involving the microwave heating of a substrate, saturated with a precursor solution to form a thin layer of zeolite nano seeds and subsequent hydrothermal treatment to crystallize MFI zeolite on the porous support. MFI films were prepared on cordierite honeycomb substrates and alumina disks. A uniform 75 μm thick zeolite film was produced by this method after 6 h of hydrothermal treatment preceded by microwave heating for 10 min. The amount of zeolite film formed on a honeycomb substrate by 10 min of microwave heating followed by 12 h of hydrothermal treatment was equivalent to that formed in 24 h by conventional hydrothermal treatment. The BET surface area of these samples was more than double that of samples made by conventional hydrothermal synthesis. An increase in the microwave heating time produced denser but smaller zeolite crystals where as an increase in the microwave power produced smaller numbers of larger crystals. Faster and more efficient zeolite film formation results from factors including saturation of the substrate with a greater amount of precursor, the formation of zeolite nuclei during microwave heating and enhanced subsequent growth of zeolite on these nucleation sites during hydrothermal treatment.

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