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Microwave-assisted hydrothermal synthesis of zeolite Beta coatings on ALD-modified borosilicate glass for application in microstructured reactors

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Abstract

Stable zeolite Beta coatings with a thickness of 1–2 μm were synthesized on a borosilicate glass substrate by microwave-assisted hydrothermal synthesis. Prior to the synthesis, surface roughness of the substrate was increased to 1.0 μm. Then, two thin films of zirconia and titania were successively deposited at 300 °C on the glass substrate by atomic layer deposition using $ZrCl_4$ as metal precursors for zirconia and $TiCl_4$ for titania, respectively. Oxygen and H_2O were used as oxygen precursors in the ALD process. The internal zirconia film protects the glass substrate from dissolution in a highly alkaline synthesis solution. The outer titania film was made superhydrophilic (>15 OH/nm^2) by an UV irradiation, which enhances the nucleation and crystallization processes on the substrate. The duration of the zeolite nucleation period was decreased by using the additive effect between fluoride ions and the zeolite seed solution under microwave irradiation. A uniform zeolite Beta coating was obtained already after 8 h at 150 °C in a microwave from a precursor gel with $SiO_2/Al_2O_3 = 25$, $TEAOH/Al_2O_3 = 8.75$, $H_2O/SiO_2 = 11.6$, $NH_4F/SiO_2 = 0.2$. This is almost six times faster comparing to conventional hydrothermal synthesis.

Keywords: ALD; Zeolite Beta; Coatings; Microwave synthesis; Borosilicate glass

1. Introduction

Application of zeolitic coatings improves the performance of supported catalysts, as demonstrated in the case of membrane reactors [1], distillation units [2], adsorbents [3,4], catalytic packings [2], monoliths [5], and DeNOx reactors [6,7]. Incorporation of zeolitic coatings to microstructured reactors has also been demonstrated for various applications [6,8,9]. The three-dimensional large pore zeolite Beta (BEA) is nowadays applied in a variety of catalytic gas and liquid phase processes such as alkylation and acylation of aromatics [10,11], selective hydrogenations [12], and fine chemicals synthesis [11]. The hydrothermal synthesis of zeolite Beta coating is described on different molybdenum and titania substrates [8,13,14].

High-speed synthesis with microwaves has attracted a large attention in recent years due to considerable enhancement of reaction rates, especially in the area of organic synthesis [15]. Recently, Kim et al. have demonstrated that microwave-assisted hydrothermal synthesis (MAHyS) with NH_4F as mineralizing agent results in a highly crystalline zeolite Beta (91% crystallinity) after 8 h at 150 °C [16]. The coupling of microwave heating with a hydrothermal synthesis requires application of special non-polar substrate materials such as quartz, pure aluminium oxide (corundum), special glass types, and plastics. While these are not exotic materials for making microreactors and indeed have been applied for laboratory prototypes, there is presently no clear methodology how to perform in-situ hydrothermal synthesis of zeolitic coatings on such substrate materials. Pyrex glass is considered to be an ideal support for zeolitic coatings in a liquid phase chemical synthesis. It has a high corrosion resistance, low coefficient of temperature expansion, and it is chemically inert towards many organic molecules. Furthermore, microchannels with a precise control

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of cross-section and surface roughness can be etched in glass by dry reactive ion etching. However, zeolite synthesis usually takes place at elevated temperatures (above 130 °C) in a highly alkaline solution for several days. At these conditions, glass substrates would be completely dissolved during the synthesis. Therefore, an approach for the development of glass based microstructured devices is to utilize the intrinsic properties of glass through application of thin protective films, consisting of more alkali-resistant materials, e.g. zirconia, on the glass surface. The wettability can be improved by surface treatments or by deposition of a titania hydrophilic film, which can be made superhydrophilic (>15 OH/nm^2) by UV irradiation [8,17,18]. The goal of this work is the development of microwave-assisted hydrothermal synthesis (MAHyS) of zeolite Beta (BEA) [19,20] coatings on glass substrates to obtain a 1 μm uniform layer.

2. Experimental

2.1. Substrate modification

The experiments were carried out on 10×10 mm^2 surface modified glass substrates with a thickness of 1 mm. The surface roughness of the glass substrates was increased to ca 1000 nm by sand-jet blasting [21]. Then, the zirconia and titania thin films were grown in a low pressure flow-type ALD reactor [22]. Each of the periodically repeated growth cycles included a metal precursor pulse, purge time, oxidant pulse, and another purge time. Pulsing times were 1 s and purging times were 2 s in both processes. The zirconia films with a thickness of 750 nm were grown at 300 °C by using $ZrCl_4$ and H_2O as the ALD precursors in a flow of pure nitrogen gas [22,23]. The deposition rates were ca. 0.05 nm/cycle. The titania films with a thickness of 200 nm were grown at 300 °C by using $TiCl_4$ and H_2O as precursors. All ALD treated substrates will be referred to according to the thickness of both zirconia and titania layers. Just before the synthesis, the TiO_2 was made superhydrophilic by UV irradiation for 3 h at room temperature in a metal box (UV lamp: Hanovia 679A-36, 450 W, λ range: 220–1400 nm). The contact angle of a water droplet on the modified substrates was still below 1° up to 20 h after UV irradiation.

2.2. Microwave-assisted and hydrothermal synthesis

Zeolite Beta was synthesized in the presence of nanocrystal seed solution and fluoride ion under microwave irradiation. The zeolite nanocrystals were synthesized at 100 °C for 6 days from a solution of 94 SiO_2:1.0 Al_2O_3:1.35 Na_2O:33.5 TEAOH:1100 H_2O [24,25]. The solid product obtained was identified as the BEA structure having approximately 200 nm size. 20 μl of a 4 wt.% aqueous colloidal suspension of zeolite Beta nanocrystals was deposited by washcoating on the substrate. The pre-seeded substrates were dried at 90 °C for 10 min and then placed in the synthesis gel parallel to the gravity vector. The synthesis gel was prepared with a composition of 25 SiO_2:1.0 Al_2O_3:13.6 Na_2O:8.75 TEAOH:5 NH_4F:290 H_2O [16]. The silica and alumina solutions were prepared separately. Colloidal silica (40%, Aldrich) and tetraethyl ammonium hydroxide (TEAOH, 40% Fluka) were mixed under continuous stirring. Sodium aluminate (Riedel-de Haën) was dissolved in demineralised water and added dropwise into a silica mixture under vigorous stirring. NH_4F (Sigma–Aldrich, 99.99%) was then added and the mixture was stirred for 30 min at room temperature. The resulting gel of 50 g of was loaded in a PEEK insert which was placed in a Teflon autoclave. The autoclave was fixed tightly and placed in the microwave (MicroSYNTH, maximum power of 300 W). The temperature was measured via an opening in the autoclave. For comparison, zeolite Beta from the gel composition of 47 SiO_2:Al_2O_3:2.33 Na_2O:1.17 K_2O:24 TEAOH:658 H_2O was prepared at 130 °C under hydrothermal conditions. After hydrothermal synthesis, the coated substrates were rinsed with demi-water and placed into an ultrasonic bath (45 Hz) for 20 min to remove poorly bonded material. Then, the substrates were dried overnight at 110 °C, calcined in an air flow for 12 h at 500 °C with a heating rate of 1 °C/min.

2.3. Characterization

The substrate surface roughness (R_a) was determined by laser scanning confocal microscopy (LSCM). The hydrophilicity of the titania films was evaluated by measuring the contact angle of water on the titania films using an automatic contact angle meter (Data Physics OCA 30 equipment). A droplet of demineralized water of 2.0 μl was dropped on the surface of the substrate. The contact angle of the water droplet with the substrate was determined at room humidity of 40% with the SCA 20 software.

The synthesized coatings and powders were examined by X-ray diffraction (XRD) for phase identification and crystal orientation. XRD data were collected on a Rigaku Geigerflex diffractometer using Cu Kα radiation (1.5405 Å). XRD patterns were recorded in the range of 5–50° 2θ using step scanning at 0.02° 2θ per step and a counting time of 4 s for each step. The intensity of the peaks at the 22–25° 2θ range after 48 h was taken as standard for calculation of the crystallinity. The coating surface coverage and crystal morphology were examined by scanning electron microscopy (SEM) using a JEOL JSM-840A microscope. BET surface area and pore volume were measured with an ASAP-2000 Micromeritics equipment. The size of nanosized zeolite Beta particles was measured by dynamic light scattering (DLS) with a Malvern 4700 apparatus.

3. Results and discussion

A 750 nm zirconia protective film was found to be stable in an alkali-containing mixture with a total hydroxyl concentration of 1.1 M at 150 °C for at least 8 h. However, a noticeable dissolution of the glass substrates was observed already after 10 h. From a practical point of view, the ALD time above 25 h (resulting in a 750 nm zirconia film) is not feasible to apply, among others due to a non-uniform growth of the film after a large number of ALD cycles. Therefore, to shorten the synthesis time to at most 10 h, the duration of the nucleation period was decreased by using the additive effect between fluoride ions and the zeolite seed solution in MAHyS.

A zeolite Beta coating with a low crystallinity is obtained after 8 h under microwave irradiation. The crystallinity increases by 40% after pre-seeding of the substrate with zeolite Beta nanocrystals as shown in Fig. 1.

This confirms that seeds profoundly accelerate the crystallization rate. Almost complete crystallization of the BEA structure is achieved after 10 h with the combination of fluoride ions and seeding under microwave irradiation. Before the synthesis, the adhesion between the nanocrystals and the substrate was rather weak as they were completely removed after ultrasonication. The adhesion between the nanocrystals and the substrate was profoundly improved after MAHyS as shown in Fig. 2.

A multilayer of intergrown crystals with an average crystal size of 500 nm is observed on the substrate. The crystal size is 2.5 times larger than the size of the zeolite-nanocrystal seeds demonstrating that crystallization continues on the seeds. Additional cross-linking with the surface hydroxyl groups of the substrate is created in the course of crystallization. Without pre-seeding of the substrate with zeolite Beta nanocrystals, the complete coverage of the substrate has still not been achieved (Fig. 3).

For comparison, zeolite Beta was prepared under conventional hydrothermal synthesis at 130 °C. Based on the published data [8,13], the total OH concentration was fixed at 1.0 M, and the ratios of $H_2O/Si = 14$ and $(Na + K)/Al_2O_3 = 7$ were applied. To avoid severe dissolution of the glass substrates, NaOH was not used in the synthesis, even though its application as mineralizing agent was often reported in literature. To prevent glass dissolution a forced heating method was applied [26] which allowed decreasing the synthesis time in all hydrothermal in-situ syntheses.

The synthesis of zeolite Beta coating by in-situ hydrothermal synthesis was performed with the TEA/Al_2O_3 ratios in the range from 20 to 24 to provide the shortest synthesis time [13]. Higher synthesis temperatures resulted in a substantial dissolution of the glass substrates with the protective zirconia layer. The influence of the TEA/Al_2O_3 ratio on the XRD crystallinity and adhesion of coatings with Si/Al ration of 23.5 was investigated. The synthesis was performed at 130 °C for 48 h with TEA/Al_2O_3 ratios of 20, 22 and 24.

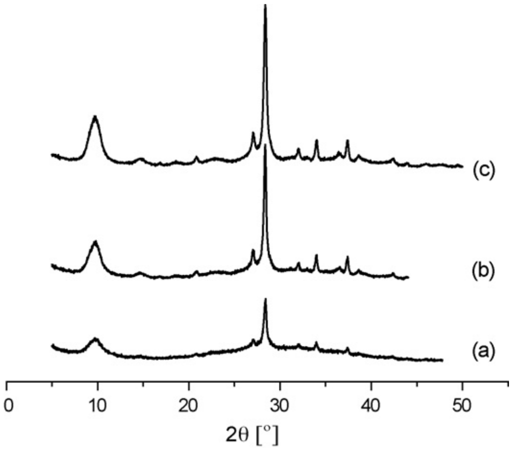

Fig. 1. XRD patterns of zeolite Beta coating after microwave-assisted hydrothermal synthesis at different synthesis time: (a) 8 h, without pre-seeding; (b) 8 h, with pre-seeding and (c) 10 h without pre-seeding.

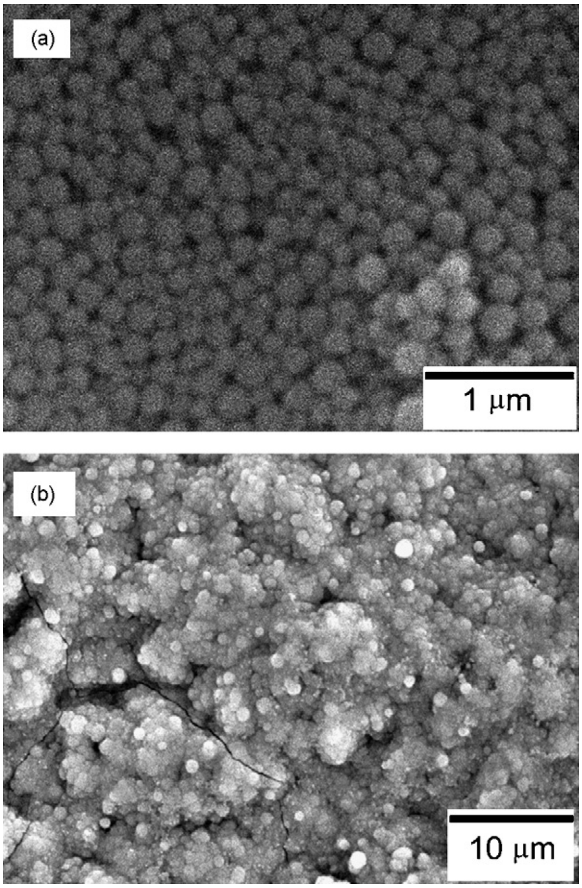

Fig. 2. SEM images of zeolite Beta films on a borosilicate glass substrate: (a) pre-seeded nanocrystals and (b) zeolitic coating after MAHyS. The synthesis was performed from a solution with a composition 25 SiO_2:1.0 Al_2O_3:13.6 Na_2O:8.75 TEAOH:5 NH_4F:290 H_2O at 150 °C for 8 h.

The corresponding SEM images of the coatings are shown in Fig. 4. The coatings with TEA/Al_2O_3 ratios of 20 and 22 show weak adhesion. No zeolite Beta crystals were present on the glass substrate after 30 min ultrasonications. On the contrary, a uniform zeolite Beta coating with high adhesion was obtained at

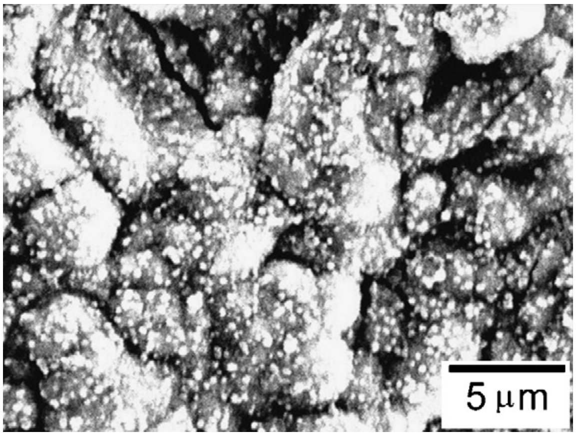

Fig. 3. SEM imag of zeolite Beta on borosilicate glass by MAHyS without pre-seeding by nanocrystals. The solution composition was 25 SiO_2:1.0 Al_2O_3:13.6 Na_2O:8.75 TEAOH:5 NH_4F:290 H_2O at 150 °C.

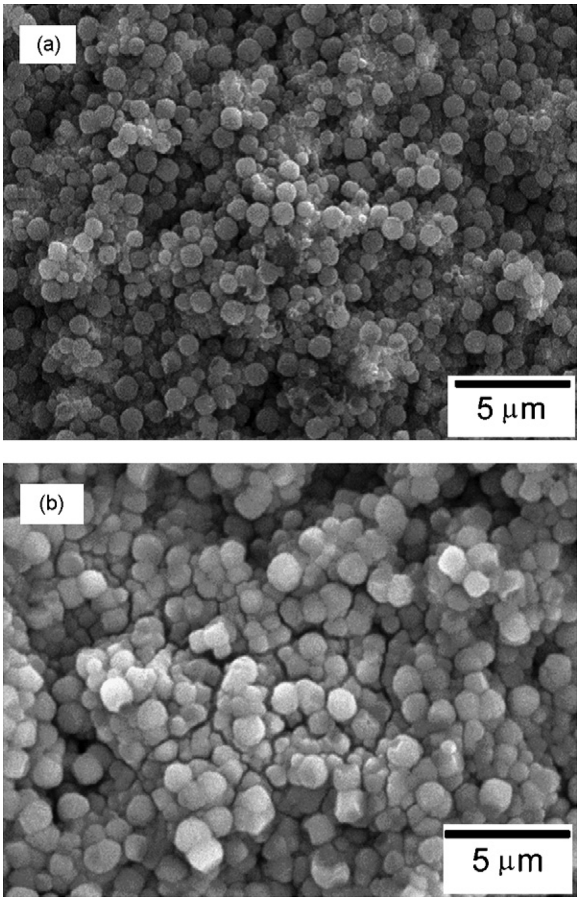

Fig. 4. SEM images of zeolite Beta coating on a borosilicate glass substrate prepared by conventional hydrothermal synthesis at 130 °C (a) TEA/Al_2O_3 = 20 and (b) TEA/Al_2O_3 = 24. The solution composition was 47 SiO_2:1.0 Al_2O_3:2.33 Na_2O:1.17 K_2O:24 TEAOH:658 H_2O.

a TEA/Al_2O_3 ratio of 24. Further increase in TEA/Al_2O_3 gave a low coverage of the zeolite Beta coating.

4. Conclusions

Microwave-assisted hydrothermal synthesis (MAHyS) and conventional hydrothermal synthesis of zeolite Beta coatings on a borosilicate glass substrate have been carried out. A 750 nm zirconia layer, deposited by atomic layer deposition (ALD) from the $ZrCl_4$ and H_2O precursors, provided a good protection of the glass substrate during the synthesis in a highly alkaline solution. The coatings with an average crystal size of 500 nm have been obtained in MAHyS. The synthesis time was decreased to 8 h at 150 °C by using the additive effect between fluoride ions and the zeolite seeds with an average particle size of 200 nm. In the absence of microwave, the hydrothermal in-situ synthesis of zeolite Beta coatings required several days at 130 °C. Higher synthesis temperatures resulted in a substantial dissolution of the glass substrates with the protective zirconia layer. The effect of synthesis conditions was investigated to decrease the synthesis time of the coating with the Si/Al ration of 23.5. The fully crystalline coatings with a high adhesion to the substrate were obtained after 48 h from a synthesis mixture with template to alumina ratio of 24.

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