Continuous Flow Synthesis of a ZSM-5 Film in Capillary Microchannel for Efficient Production of Solketal

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1. INTRODUCTION

Microreactor is considered as a revolutionary technology in the future chemical industry, which can realize the safe, flexible, green, and efficient chemical reaction based on the "micro" characteristics and intrinsic process intensification function.1-4 Especially, in continuous flow heterogeneous catalysis, it can effectively improve the reaction process due to the large surface-area-to-volume ratio of the microchannel and enhance mass transfer and heat transfer rates.5-7 However, some structure and size limitations are negative for wide use in facial industrial production. One of which is that its specific surface area is still about 3 orders of magnitude smaller than that of nanoporous catalyst particles.7 Therefore, encapsulating rich porosity and high surface area catalysts or catalyst supports becomes necessary from an actual chemical production point of view.9-12

Zeolite is an ideal modification material, which has inherent catalysis, separation, adsorption performance, and good physical/chemical stability. Zeolites have a wide range of applications in the field of chemical production such as catalysis and separation.13-15 Up to date, wall-coated zeolite membrane microreactor has shown attractive prospects in continuous flow heterogeneous catalysis.16-19 On one hand, wall-coated microchannel can maintain well-defined flow geometries and fluid dynamics properties, which could ensure smooth flow of reagents without leading to any adverse pressure drop or blockage of microchannels.12 On the other hand, it constitutes a powerful tool of typically defined membrane microreactor (MMR) to carry out catalytic reaction and separation process in a single step,18 which can combine the advantages of zeolite catalysis, membrane separation, and microreactor technology. It has become a new direction and challenge in the field of microchemical technology.20

The traditional construction of the zeolite membrane microreactor system is mainly divided into two steps. First, the uniform and continuous high-crystallinity zeolite membrane has to be prepared by static secondary hydrothermal synthesis of zeolite film. Second, the microchannel and peripheral components are combined into a microreactor system by microprocessing technology.21 Yeung22,23 and Zhang24,25 had carried out the research on the design and reaction performance of zeolite membrane assembled microreactors such as Zeolite Socony Mobil-5 (ZSM-5), Sil-1, NaX/NaA, and NaY/NaA in stainless steel microchannel. These zeolite membrane microchannel reactors were used in the condensation of benzaldehyde and ethylcyanoacetate, and the conversion was significantly higher than the traditional fixed-bed reactor. However, in the case of some...
capillary microchannels with high length-to-diameter ratio (>100) or closed plate/chip microchannel devices in which the postassembly of the microchannel is not feasible, it is difficult to prepare uniform and continuous zeolite membrane with controllable thickness and firm combination by the traditional membrane preparation method. The continuous flow method, defined as microfluidic technology, can solve these problems. Nanofilm deposition in microchannel and fabrication of zeolitic imidazolate framework-8 (ZIF-8) molecular sieving membranes in hollow fiber has come true with this easily scalable, reliable, and benign flow fabrication process. Our previous works further present that the zeolite faujasite-X (FAU-X) and ZIF-8 films can be prepared in a capillary microchannel by continuous flow hydrothermal synthesis, and fine control of the film thickness can be readily achieved by adjusting the flow time. Unfortunately, this field of continuous flow processing of zeolite films in closed microchannel reactors has not been sufficiently explored, besides the only retrievable literature.

In this work, the secondary hydrothermal growth with continuous flow feeding strategy was described for the preparation of ZSM-5 zeolite film in high length-to-diameter ratio capillary microchannel. The parameters of length-to-diameter ratio, seed coating, feed flow rate, and synthesis time were studied. And then, the hydrogen form of the ZSM-5 (HZSM-5) zeolite film capillary microreactor with the acid catalytic function was constructed to study the solketal (1:1,1,2-isopropylideneglycerol, C₆H₁₂O₃) production from the ketalization reaction of glycerol with acetone. This work would give out some scientific references for the construction of catalytic zeolite film microchannel reactors with a high length-to-diameter ratio and their application in the high-value conversion of biomass glycerol.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. The quartz capillaries (internal diameter (i.d.) 0.53 and 0.32 mm, length 100 mm) were purchased from Dalian Zhonghuida Scientific Instrument Corporation. The chemical reagents included tetratrapropylammonium hydroxide solution (TPAOH, ~50 wt % in water), tetraethyl orthosilicate (TEOS, wt % ≥99.5%), sodium aluminate (NaAlO₂, wt % ≥99.0%), sodium hydroxide (NaOH, wt % ≥96.0%), anhydrous alcohol (EtOH, wt % ≥99.7%), ammonium acetate (NH₄Ac, wt % ≥98.0%), sodium sulfate (Na₂SO₄, wt % ≥99.0%), acetone (marked as ACT, wt % ≥99.5%), glycerol (marked as GCR, wt % ≥99.0%), and N,N-dimethylformamide (DMF, wt % ≥99.5%) were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). The used chemical coupling agent of (3-aminopropyl) trimethoxysilane (APTMS, ~97 wt %) was purchased from Aladdin Industrial Corporation (Shanghai, China). All the above used chemical reagents were analytical reagent (AR) and used as received without further purification. The used deionized water (DI water, 18.2 MΩ) was homemade.

2.2. Continuous Flow Preparation of ZSM-5 Film in Capillary Microreactor. 2.2.1. Synthesis of ZSM-5 Crystal Seed. The ZSM-5 zeolite crystal seed was synthesized according to our current work. First, 6.5023 g of TPAOH as the template agent was mixed with 34 mL of DI water. Second, 5.0 mL of EtOH was added and stirred for 10 min. And then, 0.1224 g of NaAlO₂ as the aluminum source was dumped and stirred until a clear solution was obtained. Finally, 11.3 mL of TEOS as the silicon source was added dropwise at room temperature and stirred until the mixture was completely clarified. After aging for 6 h, the above mixture solution was transferred in a Teflon-lined autoclave to crystallize for 14 h at 120 °C. After the crystallization was completed, the autoclave was cooled down with large amounts of tap water. The products were centrifuged and washed with large amounts of DI water until the pH was <8. After then, DI water was replaced with large amounts of EtOH and 1.0 wt % ZSM-5 seed suspension was prepared for later use.

2.2.2. Fabrication of ZSM-5 Film in Capillary Microchannel. The preparation of ZSM-5 zeolite film in the capillary was carried out on a home-made device shown in Figure 1.

The whole device was connected with a silicone rubber tube to form a well-sealed continuous flow system. The liquid solution was pumped into the capillary microchannel with a constant flow rate by a peristaltic pump (BT100-2J, Baoding Longer Precision Pump Co., Ltd., China). The synthesis temperature was controlled by the self-contained thermostat. The entire synthesis procedure included four steps: In the first step, the capillary was pretreated by pumping 0.5 mol/L NaOH solution at 95 °C for 1 h. Then, large amounts of DI water were used to wash the capillary and dried at 100 °C for 1 h. For the second step, the APTMS modified capillary was achieved by continuous pumping the 1:15 (V/V of APTMS/ EtOH) dispersion liquid at a constant flow rate of 1.65 mL/h. The temperature was kept at 60 °C for 2 h. After then, the residual APTMS was completely replaced by amounts of EtOH. For the third step, the ZSM-5 crystal seed layer was coated in the APTMS modified capillary by pumping 1.0 wt % ZSM-5 seed suspension with a constant flow rate of 1.65 mL/h. The temperature was kept at 60 °C for 2 h. After then, the residual ZSM-5 crystal seeds were cleaned with amounts of EtOH and the seed-coating capillary was dried at 100 °C for 1 h. For the fourth step, the ZSM-5 zeolite film was synthesized in the seed-coating capillary by continuously pumping the film synthetic solution. The film synthetic solution was a compound of 2.0335 g of TPAOH, 5.4 mL of TEOS, 0.0425 g of NaAlO₂, 65 mL of DI water, 8.3 mL of EtOH, and 0.2800 g of Na₂SO₄ with a molar ratio of 0.2TPAOH/SiO₂/0.016Al/150H₂O/6EtOH/10Na₂SO₄. TPAOH was first mixed with DI water and then EtOH and TEOs were added in the order. After stirring for 4 h, NaAlO₂ and Na₂SO₄ were added in turn. After stirring at room temperature for 1 h, a clear solution was obtained and transferred in a Teflon-lined autoclave to crystallize at 100 °C for 12 h. The above precrystallization film synthetic solution was pumped into the seed-coating capillary at a constant flow rate. The synthesis temperature was maintained at 98 °C for several hours (alteration of feed flow rate and synthesis time was according to experimental
conditions). Finally, the ZSM-5 film capillary was fabricated by washing with large amounts of DI water and drying at 40 °C for 12 h.

2.3. Characterization. The powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation to identify the ZSM-5 zeolite crystalline phase. The working voltage and current were 40 kV and 40 mA. The scanning rate and range (2θ) were 5 °/min and 5–60°. Scanning electron microscope (SEM) images of ZSM-5 crystal seed and film morphology were inspected with a JSM-7500F cold field emission scanning electron microscope (JEOL, Japan). The acceleration voltage and working current were 5 kV and 20 mA. All samples were coated with gold before measurements.

The particle size distribution of the ZSM-5 crystal seed was conducted in the continuous flow reaction device shown in Figure 2. Reactants of glycerol and acetone were fed respectively in a self-made annular tube micromixer by two peristaltic pumps (BT100-2J, Baoding Longer Precision Pump Co., Ltd., China) with different flow rates. After then, the reactant mixture flowing out of the micromixer was immediately pushed into the HZSM-5 film capillary microchannel. The reaction temperature was maintained at 50 °C. The feed molar ratio of glycerol to acetone was 1:2 and without using an additional solvent. The residence time was 2.86 min. As a reference, the catalytic performance of the HZSM-5 crystal seed and the NaOH-pretreated HZSM-5 crystal seed powder in a glass flask batch reactor was studied. The reaction temperature was 50 °C. The molar ratio of acetone to glycerol was 2:1 and no solvent was added. The mass ratio of powder catalyst/glycerol is 5 wt %. The products of reacted 2 h were collected and analyzed by gas chromatography (GC9790, Zhejiang Fuli Analytical Instruments Co., Ltd., China) equipping a SE-30 column (30 m × 320 μm × 1 μm) and flame ionization detector. The detection conditions were as follows: Oven temperature was 100 °C. The injector temperature was 260 °C. The detector temperature was 280 °C. Temperature program: kept at the initial oven temperature of 100 °C for 1 min. After that, the oven temperature increased to 250 °C at the rate of 10°C/min and kept for 4 min. Finally, the oven temperature reduced rapidly to 100 °C. The yield of solketal was calculated by an external standard method, in which the external standard reagent was DMF. The expression was as follows: $Y_{SKT} = \frac{A_{SKT} \times m_{DMF} \times M_{GLY}}{A_{DMF} \times m_{GLY} \times M_{SKT}} \times 100%$

3. RESULTS AND DISCUSSION

3.1. Characterization of ZSM-5 Seed Coating. Based on the previous work, the internal surface of the used quartz capillary is inactive and not helpful for direct film growth by in situ hydrothermal synthesis. The chemical coupling seeding process is favorable for preparing continuous and uniform zeolite film, as it encourages zeolite deposition and growth by providing active nucleation and crystallization sites in the following hydrothermal procedure. Meanwhile, the particle size and uniformity of the crystal seed are equally crucial for the fabrication of a well-intergrown zeolite film. Therefore, as shown in Figure 3a, the nanosized ZSM-5 crystal seed was prepared in this work. The particle size distribution posed in Figure 3b revealed that the synthesized ZSM-5 crystal seed was uniform with a particle size of around 250~300 nm, which was in agreement with the SEM image of Figure 3a. The XRD pattern shown in Figure 4 further confirmed that the synthesized crystal seed was the pure ZSM-5 crystal phase. Figure 3c,d shows the SEM images of the ZSM-5 seed coating on the inner wall of the capillary with internal diameters of 0.32 and 0.53 mm, respectively. It revealed that the continuous flow chemical coupling process could bond uniform zeolite seed coating to the inert and smooth quartz capillary surface, which played an important role in the subsequent induced film formation. Furthermore, a comparison of Figure 3c,d further reveals that the microchannel with a smaller internal diameter (higher length-to-diameter ratio) was more favorable for the coating of a uniform seed layer. The results inferred that the microchannel showed excellent hydrodynamic properties.

3.2. Characterization of the ZSM-5 Film. The ZSM-5 film synthesized by the following continuous flow secondary hydrothermal growth is shown in Figure 4. As shown in Figure 4a, using a clear solution rather than a precrystallization film synthetic solution, the cross-sectional SEM image showed a continuous film appearance with dense particle deposition coating compactly adhered to the capillary inner wall. This appearance of a dense deposition coating layer could be obviously verified by the inset SEM image of surface...
morphology in Figure 4a. While using the precrystallization film synthetic solution, as shown in Figure 4c,d, both the SEM images presented continuous and well intergrowth film morphology with compactly adhering on the capillary inner wall. The XRD patterns in Figure 4b identified the synthesized film as ZSM-5. These results inferred that the continuous flow secondary hydrothermal growth method was an effective route to prepare a well-crystallized ZSM-5 film in the capillary microchannel with a high length-to-diameter ratio. A careful comparison of the SEM images of the ZSM-5 film prepared in 0.53 and 0.32 mm capillary microchannels, which are shown in Figure 4c,d, revealed that the microchannels with smaller internal diameter (higher length-to-diameter ratio) tended to have a uniform and compact film morphology. This study believed that the inherent enhancement of the mass/heat transfer rate and excellent hydrodynamics properties of the microchannels were favorable for the uniform seed coating and further inducing uniform, compact, and well-crystallized film.

Figure 3. (a) SEM image of the ZSM-5 seed crystals, (b) particle size distribution of the ZSM-5 seed, (c) SEM image of seed coating in 0.32 mm capillary, and (d) SEM image of the seed coating in 0.53 mm capillary.

Figure 4. (a) SEM images of the ZSM-5 film prepared by clear film synthetic solution. (b) XRD patterns of the ZSM-5 seed and capillary films prepared by precrystallization film synthetic solution. (c) SEM images of 0.53 mm capillary film prepared by precrystallization film synthetic solution. (d) SEM images of 0.32 mm capillary film prepared by precrystallization film synthetic solution.
3.3. Influence of Feed Flow Rate. Feed flow rate is one of the critical factors in continuous flow hydrothermal synthesis of the zeolite film in a capillary microchannel.\textsuperscript{34} The feed flow rate is related to the residence time and flow line velocity of the synthetic liquid in the microchannel and then affects the contact time and axial shear force between the flowing liquid and the inner wall of the microchannel. In this work, the influence of the feed flow rate on the ZSM-5 film thickness was studied in this continuous flow capillary system with internal diameters of 0.53 and 0.32 mm. The synthesis temperature was 98 °C, and the synthesis time was 24 h. As shown in the cross-sectional SEM images of Figure 5, films of different thicknesses with the continuous, well-crystallized appearance and compactly adhered to the capillary inner wall were prepared in both 0.53 and 0.32 mm capillary microchannels. The corresponding fitting plots of Figure 6 reveal that the film thickness increased slightly with the increase of the feed flow rate. With the decrease of the capillary internal diameter (the increase of the length-to-diameter ratio), the increasing trend was less obvious, which was different from our previous work.\textsuperscript{34} The reason might be that the growth of the ZSM-5 crystal was slow at low temperature (98 °C in this work), and the epitaxial growth of seed layer was not disturbed by the axial shear force when this continuous flow system used the feed of precrystallization film synthetic solution, which resulted in the approximate film thickness.

3.4. Influence of Flow Synthesis Time. Flow synthesis time, defined as the time on stream (TOS), is another critical factor in the continuous flow synthesis system of a molecular sieve film.\textsuperscript{30−32} In this work, the effect of flow synthesis time on the film thickness was investigated in this continuous flow capillary system with internal diameters of 0.53 and 0.32 mm. The synthesis temperature was 98 °C, and the feed flow rate was 0.54 mL/h. As shown in the cross-sectional SEM images of Figure 5 and the fitting plots of Figure 8, all of the results revealed that the film thickness in capillary microchannels with different internal diameters presented linear increasing trend with the flow synthesis time, which was similar to the traditional static hydrothermal synthesis. Therefore, the growth of the ZSM-5 film in the capillary microchannel could be precisely controlled by adjusting the flow synthesis time to obtain different film thicknesses. In addition, the fitting plots of film thickness as a function of flow synthesis time in Figure 8 reveal that the increasing rate of film thickness with the flow synthesis time (slope of film thickness vs time on stream) was different in the 0.53 and 0.32 mm capillary microchannels. The increasing rate of film thickness vs flow synthesis time was smaller in a capillary microchannel with smaller internal diameter (higher length-to-diameter ratio), and the film morphology tended to be more compact and continuous. It reflected the excellent hydrodynamic performance of the microchannels in the continuous liquid flow process.

3.5. Catalytic Performances of the HZSM-5 Film Capillary Microreactor. The ketalization reaction of glycerol with acetone to produce solketal has been studied as an acid-catalyzed reaction. Also, the catalytic performance of various solid acid catalysts such as Amberlyst-35,\textsuperscript{35} H-BEA, H-MFI, H-MOR,\textsuperscript{36−38} and resin Lewatit GF101\textsuperscript{39} has been investigated in a batch reactor. As one of the economic utilization processes for transforming glycerol to various value-added chemicals in the biodiesel industry, a continuous-flow reactor is a suitable alternative of batch reactor based on the common drawbacks when scaling up the process.\textsuperscript{40} However, in consideration of glycerol’s high viscosity, particularly at low temperatures and solubility with other reactants, the continuous flow fixed-bed reactor suffers from a high-pressure drop, low conversion, and catalyst clogging the

![Figure 5](https://example.com/figure5.png)  
**Figure 5.** Cross-sectional SEM images of the ZSM-5 film synthesized in 0.53 mm capillary with different feed flow rates: (a) 0.38 mL/h, (b) 0.54 mL/h, (c) 0.85 mL/h, and (d) 0.925 mL/h. Cross-sectional SEM images of the ZSM-5 film synthesized in 0.32 mm capillary with different feed flow rates: (e) 0.23 mL/h, (f) 0.38 mL/h, (g) 0.69 mL/h, and (h) 0.85 mL/h.

![Figure 6](https://example.com/figure6.png)  
**Figure 6.** Plots of film thickness as a function of feed flow rate.
It seems that the microreactor combined with wall-coated heterogeneous catalysts is an effective solution. Wall-coated microreactor can not only cause rapid mixing of glycerol with other reactants under the solvent-free condition and offer extensive contact interface of liquid reactants with solid catalysts due to its intrinsically high mass transfer rate but also ensure a smooth inflow of highly viscous reagents without leading to any adverse pressure drop or blockage of the microchannel. Therefore, in this work, the acid catalytic ketalization reaction of glycerol with acetone was conducted to evaluate the catalytic performance of the HZSM-5 film capillary microreactor under continuous flow and solvent-free conditions. All of the results of solketal yield are shown in Figure 9. A comparison of (1) and (2) revealed that NaOH-pretreated HZSM-5 crystal seed powder showed a higher yield of solketal (~30%) than the HZSM-5 crystal seed powder (~15%) and commercial ZSM-5 catalyst (~20%). The reason was claimed to be that the NaOH partially dissolved the ZSM-5 framework silicon and produced mesoporous channels, which was beneficial to the mass transfer of macromolecular reactants and products in the crystal and the leakage of more acid centers. A comparison of (2), (3), and (4) presented similar single-pass yield of solketal (~30%). On one hand, the reason might be related to the enhanced mass transfer of the capillary microchannel itself. On the other hand, it inferred that the HZSM-5 film prepared in the capillary microchannel produced a hierarchical porous structure. With the aim to further confirm the pore distribution of synthetic film, N₂ adsorption–desorption isotherms at 77 K were measured and are shown in Figure 10. The adsorption–desorption isotherms with a hysteresis loop at P/P₀ > 0.4 proved that mesoporous structures were formed. The BJH adsorption pore size distributions presented that these inhomogeneous mesoporous structures were present in both HZSM-5 film capillary with an internal diameter of 0.32 and 0.53 mm.

4. CONCLUSIONS

In summary, a facile and convenient continuous flow fabrication of the ZSM-5 zeolite film in a closed capillary microchannel with the high length-to-diameter ratio is developed. Based on the premodification with crystal seed coating and continuous flow hydrothermal growth, a uniform and continuous ZSM-5 film with well intergrowth and hierarchical porous structure could be prepared in the capillary microchannels under a low temperature of 98 °C. The film thickness could be readily controlled by adjusting the feed flow rate and/or synthesis time. Using NH₄⁺ exchange under similar flow conditions, the acidic HZSM-5 film capillary microreactor was fabricated and applied in continuous flow ketalization reaction of glycerol with acetone to produce solketal. The single-pass yield of solketal could reach ~30% under mild conditions. All of the results supported this HZSM-5 film...
capillary microreactor as a highly efficient and feasible microdevice and its potential application in highly value-added utilization of glycerol by continuous flow ketalization reaction to synthesize solketal and other derivatives. Otherwise, this microfluidic processing strategy provided an extended application in the fabrication of zeolite films-based capillary microchannel with high length-to-diameter ratio or other closed chip-based microchannel devices, and thus more kinds of efficient microreactors could be achieved.

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Notes
The authors declare no competing financial interest.

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