



# Ultrafast and mesopore-free synthesis of hierarchical ZSM-5 zeolites

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## ABSTRACT

The facile synthesis of hierarchical ZSM-5 zeolites without mesoporegens is highly desirable for industrial applications. In this study, hierarchical ZSM-5 zeolites with abundant mesopores and a nearly single-crystalline structure were rapidly synthesized in a mesopore-free system. Under conventional heating, the synthesis time was significantly reduced to just 15 min, significantly improving production efficiency. The key to this ultrafast process was the use of a tubular reactor, combined with the strategic selection of silicon and aluminum sources.

## 1. Introduction

Hierarchical zeolites, which possess both intrinsic zeolitic pores and additional secondary porosity, have attracted significant attention in catalysis due to their significantly enhanced diffusion properties compared to conventional microporous zeolites [1]. The synthesis of hierarchical zeolites typically relies on various mesoporegens to induce the formation of secondary porosity [2,3]. However, this route not only increases production costs but also raises environmental concerns. Additionally, the synthesis process usually takes several tens of hours [4], further limiting the scalability of hierarchical zeolites for industrial applications.

In this study, we propose a simple and efficient route for the ultrafast, mesopore-free synthesis of hierarchical ZSM-5 zeolites. Despite the absence of mesoporegens, high-quality hierarchical ZSM-5 zeolites with abundant mesopores were synthesized in just 15 min through conventional heating. This ultrafast, mesopore-free approach effectively reduces the production cost of hierarchical ZSM-5 zeolites, making them highly attractive for large-scale applications in the chemical industry.

## 2. Experimental

### 2.1. Materials

Tetraethyl orthosilicate (TEOS) (98 %), sodium aluminate ( $\text{NaAlO}_2$ ) (56 wt%  $\text{Al}_2\text{O}_3$ , 44 wt%  $\text{Na}_2\text{O}$ ), sodium hydroxide ( $\text{NaOH}$ ) (97 %), aluminum isopropoxide (AIP) (98.5 wt%), and fumed silica (99.8 %) were purchased from Aladdin. Ludox 40 colloidal silica (40 wt%) was

supplied by Sigma-Aldrich, and tetrapropylammonium hydroxide (TPAOH) (25 wt% aqueous solution) was obtained from Innoschem.

### 2.2. Synthesis of hierarchical ZSM-5 zeolites

A silicon source (TEOS, colloidal silica, or fumed silica) was dispersed in a TPAOH solution and stirred for 12 h. An aluminum source ( $\text{NaAlO}_2$  or AIP), water, and  $\text{NaOH}$  (if needed) were mixed and stirred for 12 h, then added dropwise to the silicon solution. After stirring for 3 h, the final gel had a molar composition of  $1\text{SiO}_2: 0.033\text{Al}_2\text{O}_3: 0.033\text{Na}_2\text{O}: 0.26 \text{ TPAOH}: 50\text{H}_2\text{O}$ . The gel was transferred into a stainless-steel tubular reactor (length: 20 cm, outer diameter: 8 mm, inner diameter: 6 mm) and crystallized under autogenous pressure in a preheated oven. After the reaction, the solid product was centrifuged, washed with deionized water, and dried at  $80^\circ\text{C}$  overnight. It was then calcined at  $550^\circ\text{C}$  for 4 h to obtain the hierarchical ZSM-5 zeolite. Samples made with TEOS and  $\text{NaAlO}_2$  were labeled ZSM-5@x-y, where x and y represent the crystallization temperature ( $^\circ\text{C}$ ) and time (min), respectively. For the seed-assisted synthesis, the procedure was identical to that described above, except that 5 wt% ZSM-5 seeds (based on  $\text{SiO}_2$  in the gel), prepared according to our reported work [5], were added to the final gel, followed by an additional 30 min of stirring. The samples were labeled ZSM-5-s@x-y.

### 2.3. Characterization

Scanning electron microscopy (SEM) images were acquired using a Zeiss Merlin electron microscope. Transmission electron microscopy

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(TEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEOL TEM-2100F field-emission transmission electron microscope. X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert Powder X-ray diffractometer. Nitrogen adsorption–desorption measurements were conducted at 77 K using a Micromeritics ASAP 2460 surface area and porosity analyzer.

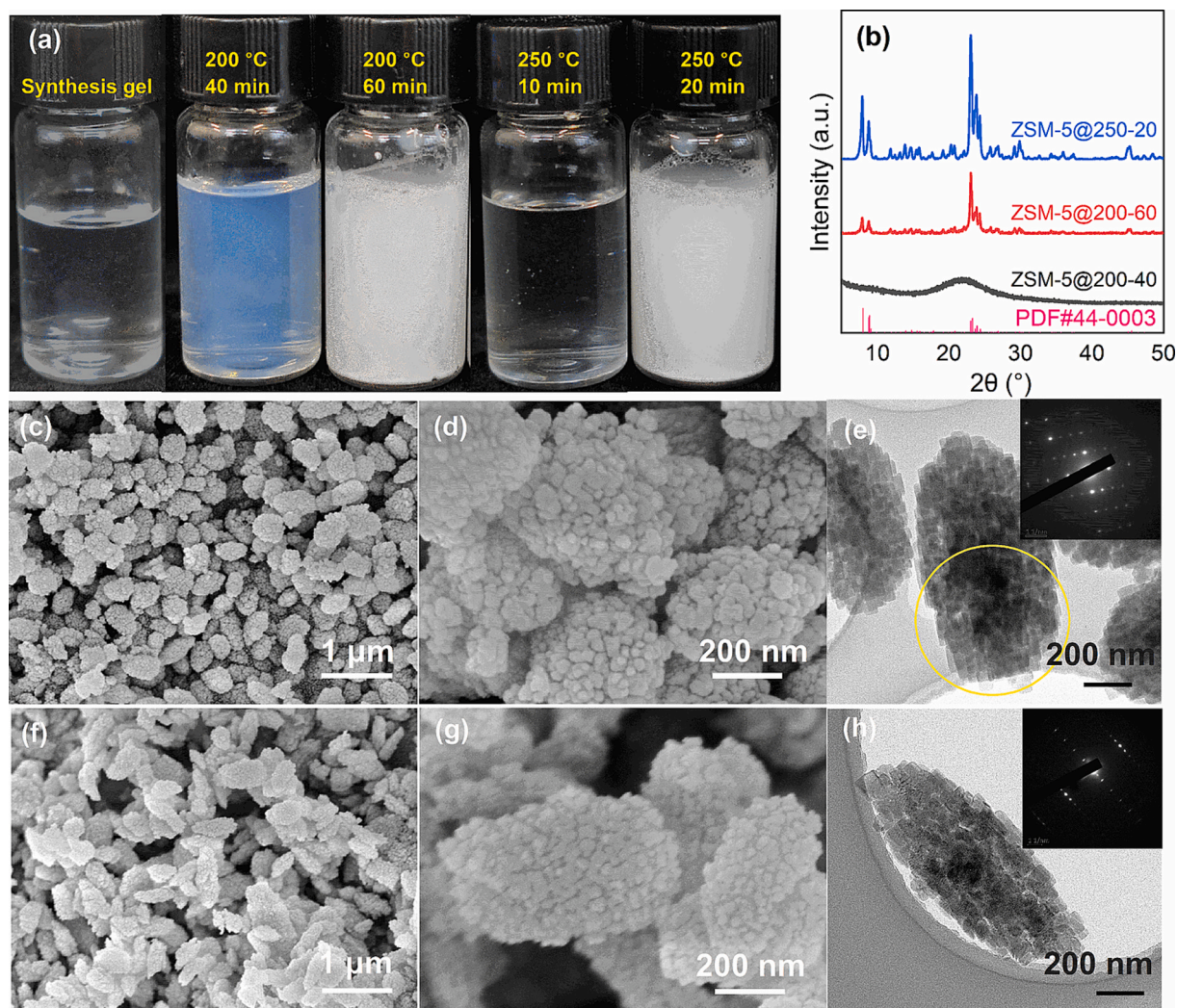
### 3. Results and discussion

Fig. 1a shows photographs of the synthesis gel, prepared using TEOS and  $\text{NaAlO}_2$  as silicon and aluminum sources, before and after hydrothermal treatment under different conditions. The initial clear synthesis gel solution was transformed into a translucent state after crystallization at 200 °C for 40 min, indicating that the hydrothermal reaction had occurred. However, the XRD pattern suggests that the collected solid product was still amorphous, implying that the reaction time was most likely insufficient. By further extending the reaction time to 60 min, the gel solution became milky white, and the solid product was successfully converted into highly crystallized ZSM-5 zeolite (Fig. 1b). SEM images (Fig. 1c and 1d) reveal that the ZSM-5 zeolite appears to be composed of aggregated nanocrystals, resulting in a mulberry-like morphology with a particle size ranging from 0.5 to 1  $\mu\text{m}$ . The TEM image (Fig. 1e) shows the presence of abundant mesopores inside the ZSM-5 zeolite particles,

further confirming the hierarchical structure of the ZSM-5 zeolite. The SAED pattern (inset in Fig. 1e) suggests that the hierarchical ZSM-5 zeolite exhibited a nearly single-crystalline structure, likely resulting from the oriented and ordered aggregation of nanocrystals that form the zeolite [6].

The synthesis time can be further shortened by increasing the crystallization temperature. When the reaction was conducted at 250 °C, the synthesis gel solution remained clear for the first 10 min, with no solid product formed. After another 10 min, the gel solution turned milky white (Fig. 1a), and the solid product was confirmed to be highly crystallized ZSM-5 crystals (Fig. 1b). SEM (Fig. 1f and 1g) and TEM (Fig. 1h) images further confirm the successful formation of a mulberry-like hierarchical ZSM-5 zeolite with a slightly elongated morphology, while maintaining its nearly single-crystalline structure (inset in Fig. 1h).

Fig. 2 presents the nitrogen adsorption–desorption isotherms of hierarchical zeolites ZSM-5@200-60 and ZSM-5@250-20, respectively. Both ZSM-5 zeolites exhibited a distinct hysteresis loop in their isotherms, indicating the presence of mesopores. As shown in Table 1, the micropore and mesopore volumes were 0.114 and 0.138  $\text{cm}^3 \text{g}^{-1}$  for ZSM-5@200-60, and 0.118 and 0.105  $\text{cm}^3 \text{g}^{-1}$  for ZSM-5@250-20, respectively. This resulted in total pore volumes of 0.252 and 0.223  $\text{cm}^3 \text{g}^{-1}$ , and BET surface areas of 348 and 344  $\text{m}^2 \text{g}^{-1}$ , respectively. These results further confirm the successful formation of a hierarchical



**Fig. 1.** (a) Photographs of the synthesis gel solution before and after hydrothermal crystallization under different conditions. (b) XRD patterns of the obtained solid products after hydrothermal treatment. SEM (c, d) and TEM (e) images of the ZSM-5@200-60 sample. SEM (f, g) and TEM (h) images of the ZSM-5@250-20 sample. The insets in (e) and (h) show the SAED patterns of the corresponding zeolite samples.



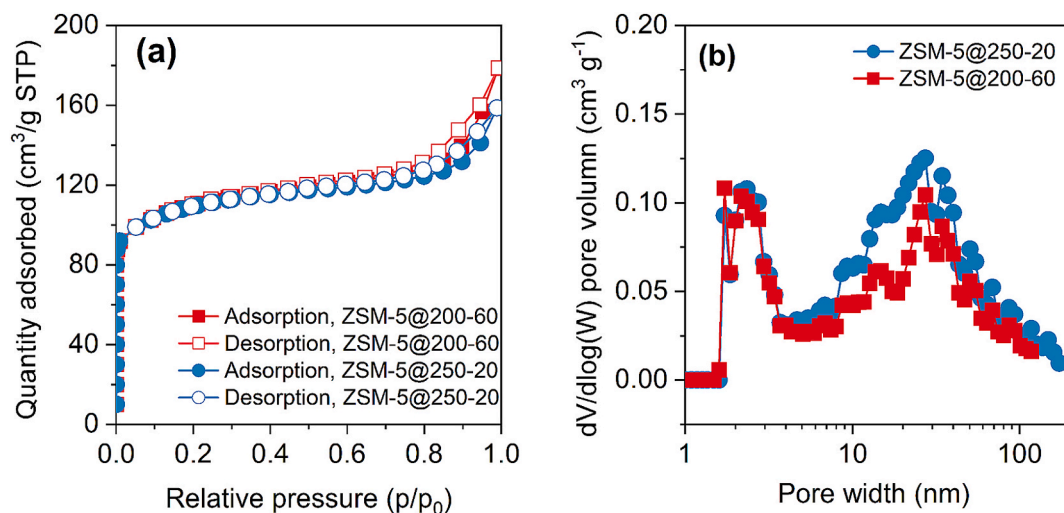


Fig. 2. (a) Nitrogen adsorption-desorption isotherms and (b) NLDFT pore size distributions of hierarchical ZSM-5 zeolites prepared under different conditions.

Table 1

Pore characteristics of hierarchical ZSM-5 zeolites.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{pore}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{meso}}$ ( $\text{cm}^3 \text{g}^{-1}$ )
ZSM-5@200-60	348	0.252	0.114	0.138
ZSM-5@250-20	344	0.223	0.118	0.105

structure in the ZSM-5 zeolites.

To further shorten the synthesis time of hierarchical ZSM-5 zeolites, we added ZSM-5 seeds (5 wt% based on  $\text{SiO}_2$ ) to the synthesis gel to accelerate zeolite nucleation. As shown in Fig. 3a, when the reaction was conducted at 250 °C, the crystallization time was further reduced to 10 and 15 min, resulting in poorly and highly crystallized ZSM-5 zeolites, respectively. This suggests that the promoting effect of the zeolite seed was minimal, and consequently, the growth of the hierarchical ZSM-5 zeolite was not effectively constrained by the nucleation step. It is worth noting that the morphology of the hierarchical ZSM-5 zeolite is similar to that in our previous study [5], where it was prepared using a conventional autoclave. However, the reaction time was significantly reduced. Therefore, the high crystallization rate can largely be

attributed to the minimal thermal lag of the stainless-steel tube reactor [7,8], as its thin-walled tubular structure facilitated rapid heat transfer to the synthesis gel, especially at high reaction temperatures. It should be noted that, after being heated in a 250 °C oven for 30 min, the temperature inside the tubular reactor reached only approximately 180 °C (Fig. S1). This indicates a significant thermal lag and suggests there is still room to further shorten the crystallization time. Additionally, it is important to note that only the combination of TEOS and  $\text{NaAlO}_2$  as silicon and aluminum sources yields highly crystallized hierarchical ZSM-5 zeolites (Fig. 3a). In contrast, when other combinations, such as TEOS and AIP, colloidal silica and  $\text{NaAlO}_2$ , or fumed silica and  $\text{NaAlO}_2$ , were used, only amorphous products were obtained (Fig. 3b), even though the reaction was conducted at 250 °C for as long as 60 min. This may be attributed to the high nucleation rate of the TEOS and  $\text{NaAlO}_2$  combination, resulting from the high solubility of both Si and Al species in the system. These findings further highlight the critical role of silicon and aluminum sources in the ultrafast, mesopore-free synthesis of hierarchical ZSM-5 zeolites.

#### 4. Conclusions

Hierarchical ZSM-5 zeolites, characterized by abundant mesopores

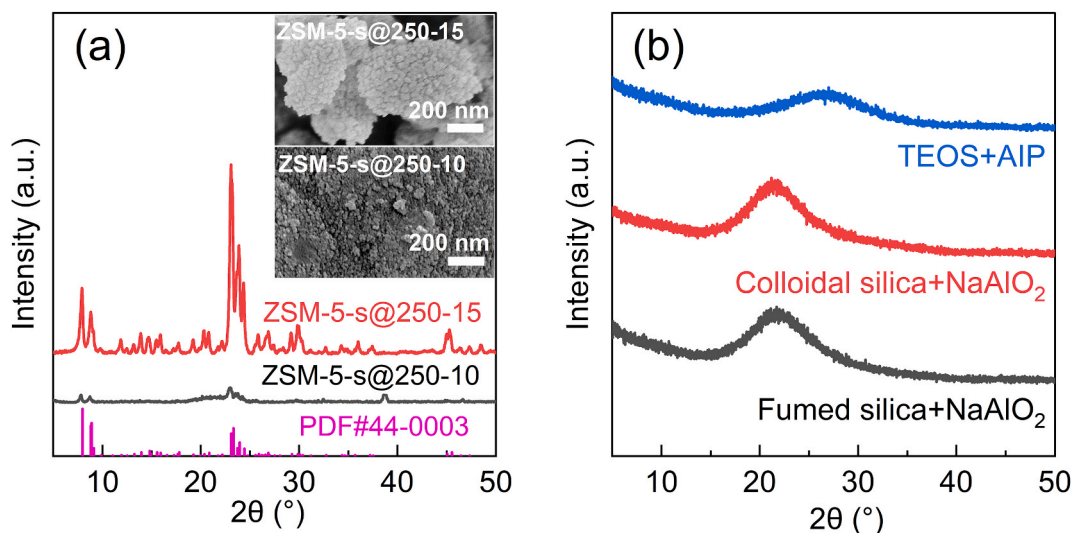


Fig. 3. (a) Photographs and XRD patterns of the obtained solid products prepared at 250 °C with adding ZSM-5 seeds. (b) Effect of silicon and aluminum sources on the synthesis of hierarchical ZSM-5 zeolites at 250 °C for 60 min.

and a nearly single-crystalline structure, can be readily synthesized without the use of mesoporegens. The crystallization time is dramatically reduced to as short as 15 min at 250 °C in a tubular reactor under conventional heating. The ultrafast crystallization of the hierarchical ZSM-5 zeolite is attributed to the optimized silicon and aluminum sources in the gel, as well as the reduced thermal lag in the tubular reactor. The preparation method developed in this study offers significant advantages in terms of rapid synthesis and mesoporegen-free conditions, making hierarchical ZSM-5 zeolites highly promising for cost-effective scaling up in industrial applications.

#### CRediT authorship contribution statement

**Feng Ye:** Writing – original draft, Investigation. **Shuanshi Fan:** Writing – review & editing. **Yanhong Wang:** Writing – review & editing. **Xuemei Lang:** Writing – review & editing. **Yihui Lv:** Investigation. **Weibo Chen:** Investigation. **Gang Li:** Writing – review & editing, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2025.138557>.

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#### Data availability

Data will be made available on request.

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