



# Ultrafast synthesis of silicalite-1 using a tubular reactor with a feature of rapid heating



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## ABSTRACT

By combining the synthesis at a higher temperature with the addition of seed, ultrafast synthesis of silicalite-1, a pure-silica zeolite with MFI structure, has been achieved in a tubular reactor that can enable a rapid heating. The synthesis period of silicalite-1 has been shortened to 10 min, while it usually takes several hours or days using the conventional methods. Estimated from crystal size, the apparent crystal growth rate of silicalite-1 was on the order of  $10^3$  nm/h for the synthesis using TEOS as a silica source, while under another synthesis condition using colloidal silica as a silica source, the apparent crystal growth rate could be as high as  $10^4$  nm/h. High crystal growth rates demonstrated that the crystallization of silicalite-1 in the tubular reactor could be very fast.

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## 1. Introduction

Zeolites are a class of crystalline inorganic materials whose pore sizes are at molecular level. Because of the featured pore dimensions together with their diversified framework topologies, zeolites have widely been used as catalysts and ion-exchangers [1–3]. New applications of zeolites are still emerging [4,5], which in turn has created new challenges for the researchers working in both fields of chemistry and engineering [6,7]. MFI zeolites can exhibit excellent performances in many fields, because of the uniqueness of MFI structure, which is composed of interconnected near-circular straight and sinusoidal channels both defined by 10-rings [8,9]. Many studies on MFI zeolites have been performed, aiming either at enhancing/extending their industrial applications or at investigating the formation mechanisms. These efforts have made MFI zeolites to be one of the most intensively studied in zeolite science. This situation is particularly true for silicalite-1, a pure-silica MFI zeolite that has been proved to be a suitable material for catalysis [10] and gas separation [11]. During the past

decades, mechanistic study on the synthesis of silicalite-1 has been enormously attempted. For example, as a classical system, the optically transparent mixture of TEOS/TPAOH/H<sub>2</sub>O (representing tetraethyl orthosilicate, tetrapropylammonium hydroxide and water, respectively) offers a possibility to perform mechanistic studies through *in situ* techniques like dynamic light scattering (DLS) [12,13] and small-angle X-ray scattering (SAXS) [14], leading to the deeper understanding of the crystallization mechanism of zeolites. Tailoring the crystal morphology of silicalite-1 using organic molecules as growth modifiers has provided useful insights into the rational design of zeolites and consequently to prompt their further applications [15,16]. These achievements undoubtedly have contributed to the development of zeolite science. Nevertheless, long time synthesis periods ranging from several hours to days are necessary for the synthesis of silicalite-1. Considering the industrial values of silicalite-1, an ultrafast synthesis/production is highly desired.

Ultrafast synthesis of silicalite-1 has never been achieved in the previous studies, except for few reports on the enhancement of crystallization rate using microwave [17,18]. Because of the drawbacks such as low controllability and limited penetration depth, however, the microwave-assisted method has unclear prospects in the practical applications. Recently, we have developed an ultrafast

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methodology to shorten the synthesis period of zeolites and zeolitic materials to several minutes or tens of minutes [19–22]. The ultrafast syntheses of several industrially important crystalline microporous materials have been demonstrated, including aluminophosphate  $\text{AlPO}_4\text{-5}$  (within 1 min) [19] and aluminosilicate zeolite SSZ-13 (within 10 min) [20,22]. Furthermore, on the basis of the ultrashort synthesis periods, continuous-flow syntheses of  $\text{AlPO}_4\text{-5}$  and SSZ-13 were demonstrated [20,21]. These results not only laid a solid foundation for developing a more efficient and economic preparation route of zeolites but also to some extent changed the traditional viewpoint that the formation of aluminophosphate and aluminosilicate zeolites is a kinetically slow process. The present work provides a case study on silicalite-1, in order to answer the question as whether the methodology of ultrafast synthesis could be applied to the pure-silica zeolites or not. Using the TEOS/TPAOH/ $\text{H}_2\text{O}$  precursor, ultrafast synthesis of silicalite-1 was attempted. By combining the high temperature synthesis in a tubular reactor with the addition of the seed, ultrafast synthesis in 10 min has been achieved. The effects of aging and synthesis temperatures were studied. Meanwhile, ultrafast synthesis of silicalite-1 using colloidal silica as a silica source was also performed, and a remarkably faster apparent crystal growth rate with respect to the synthesis using TEOS was observed.

## 2. Experimental section

### 2.1. Materials

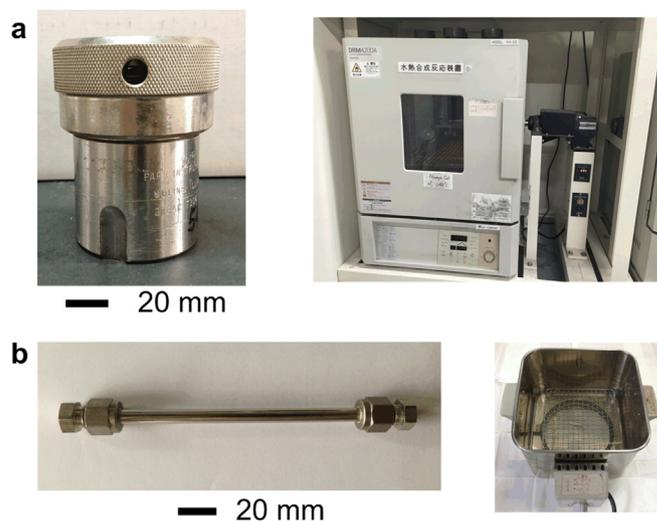
The following materials were used as received: tetraethyl orthosilicate (TEOS, >99%, Wako), tetrapropylammonium hydroxide (TPAOH, 40 wt% aqueous solution, Merck), colloidal silica (LUDOX<sup>®</sup> LS colloidal silica, 30 wt% suspension) and sodium hydroxide (1 M, Wako).

### 2.2. Synthesis of silicalite-1 seed

The seed prepared using TEOS as a silica source had the following composition: 1.0  $\text{SiO}_2$ : 4.0 EtOH: 0.25 TPAOH: 10  $\text{H}_2\text{O}$ , whereas the seed prepared using colloidal silica had a composition of 1.0  $\text{SiO}_2$ : 0.25 TPAOH: 0.12 NaOH: 20  $\text{H}_2\text{O}$ . In a typical procedure, 15 g of the synthesis gel was added to a 23 mL Teflon<sup>®</sup>-lined stainless steel autoclave (Parr, #4749) and heated at 170 °C in an air-circulating oven under rotation at 20 rpm (the autoclave and the air-circulating oven, see Fig. 1a). After heating for 24 h, the autoclave was cooled with cooling water. The product was then filtered, washed with distilled water and dried at 80 °C overnight. The synthesized silicalite-1 was used as seed without any further treatment.

### 2.3. Ultrafast synthesis of silicalite-1 in the tubular reactor

A tubular reactor, as described in the previous studies [19,20], was used for the ultrafast synthesis. As seen from Fig. 1b, all parts of the tubular reactor were made from 316L type stainless steel. 10 wt % silicalite-1 seed on the basis of  $\text{SiO}_2$  amount in the initial gel was used. The aging of the gel, if necessary, was performed at room temperature with the presence of the seed. An optimized synthesis condition could be found as follows: gel composition: 1.0  $\text{SiO}_2$ : 4.0 EtOH: 0.25 TPAOH: 10  $\text{H}_2\text{O}$ , seed amount: 10 wt% on the basis of  $\text{SiO}_2$ , and aging period: two days at room temperature prior to the high temperature synthesis. In a typical procedure, 1.5 g of the synthesis gel was transferred to the tubular reactor, which was then heated in a preheated oil bath (temperature was set at 190 °C or 210 °C, depending on the synthesis conditions; the preheated oil bath, also see Fig. 1b). After a certain period of synthesis, the tubular reactor was suddenly quenched with cooling water. The product



**Fig. 1.** Photographs of the reactors as well as the heating tools used for the synthesis of silicalite-1. a, The Teflon<sup>®</sup>-lined autoclave (left) and the air-circulating oven (right). b, The tubular reactor (left) and the pre-heated oil bath (right).

was filtered, washed with distilled water and dried at 80 °C overnight. For cleaning purpose, the tubular reactor was immersed in 1M NaOH solution and kept at 60 °C for 10 h, which was proved to be adequate to remove any nutrient residuals on the inner surface of the tubular reactor.

### 2.4. Characterizations

Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku Ultima IV diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406$  nm, 40 KV, 40 mA) at a scanning rate of 4°/min. The morphology of the products was observed by FE-SEM (JSM-7000F, JEOL, Japan) with an accelerating voltage at 15 keV. Nitrogen adsorption-desorption measurements of the calcined samples were performed on the Autosorb-1 instrument (Quantachrome Instruments) at 77 K. Before the measurements, the samples were pretreated at 400 °C for 6 h under vacuum.

## 3. Results and discussions

The synthesis of zeolites is usually conducted in Teflon<sup>®</sup>-lined autoclaves. Because of the large size and thick layers made from stainless steel and Teflon<sup>®</sup>, this kind of autoclaves inevitably leads to thermal lag (slow temperature rise). The existence of thermal lag causes a difficulty for the Teflon<sup>®</sup>-lined autoclave to perform fast synthesis on the level of minutes, as the time for thermal lag takes a time much longer to reach the targeted temperature (one to two hours, if the autoclave shown in Fig. 1a is heated in the air-circulating oven). Due to a smaller size and consequently larger surface-to-volume ratio, the tubular reactor is capable of giving a much faster temperature rise, especially when it is heated in the preheated oil bath (Fig. 1b). A comparison of temperature rising rates in tubular reactor and conventional autoclave is shown in Fig. 2. The feature of rapid heating makes the tubular reactor to be a suitable candidate of reactor to perform ultrafast synthesis, as it can avoid the thermal lag usually existing in the conventional autoclave and any negative effects along with the thermal lag.

The seeded synthesis at 210 °C in the tubular reactor significantly enhanced the crystallization rate, resulting in an ultrafast synthesis of silicalite-1 in 10 min. The synthesis of silicalite-1 is usually conducted under moderate temperatures, due to that a

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