



Synthesis of colloidal silicalite-1 at high temperatures



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ABSTRACT

Stable colloidal suspensions of silicalite-1 were prepared by hydrothermal treatment of clear precursor suspensions at high temperatures, 150 and 170 °C. The precursor suspensions were pretreated prior to hydrothermal treatment. Different pretreatment procedures were applied, namely ultrasonic treatment or heating at 45–60 °C, for different periods of time. In all cases, the size of the crystals decreased with increasing the time of pretreatment. The pretreatment procedure was found to influence the behavior of the tetrapropylammonium hydroxide solution used as structure-directing template during hydrothermal treatment. Colloidal stability of pretreated samples was improved compared to samples prepared by direct hydrothermal treatment.

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1. Introduction

Clear tetrapropylammonium (TPA) hydroxide-containing mixtures yielding colloidal silicalite-1 are probably the most-studied systems in zeolite science [1–6]. The high interest in these systems is inspired by the simplicity of the aluminum-free zeolite precursors and their homogeneity, the low synthesis temperatures employed allowing in-situ characterization by a range of advanced techniques, as well as the high reproducibility of the results. In addition to their fundamental importance, colloidal silicalite-1 crystals have been used extensively as seeds for the fabrication of supported zeolite layers and three-dimensional structures [7]. More recently, silicalite-1 seeds were employed in the revitalized seed-induced synthesis method, for preparation of nanosized ZSM-5 [8–12]. Despite the tremendous importance of systems yielding monodisperse suspensions of silicalite-1, there are technological drawbacks, such as employment of abundant amounts of expensive and toxic TPA template solutions, expensive silica sources (tetraethyl orthosilicate, TEOS), long synthesis times and low product yields, which prohibit their commercialization.

Silicalite-1 is a synthetic molecular sieve, which can only be synthesized in the presence of TPA as structure-directing agent (SDA) [13]. Monodisperse suspensions of silicalite-1 with a size of <100 nm have been prepared at temperatures below 100 °C using TPAOH in large excess. Numerous studies have looked at the mechanism of formation of silicalite-1 and how the TPA cations interact with the silicate species during ageing and crystallization

[2,3]. The effect of silicalite-1 precursors' aging for up to 30 days at ambient conditions has been studied by Li et al. [14]. Aging was found to shorten the induction and nucleation periods and crystallization times, as well as to result in smaller product crystals. The same group has developed a two-stage temperature-varying procedure, in which the precursor suspension was firstly treated at a lower temperature during the nucleation period (60 or 80 °C) followed by a rapid change of the temperature to 100 °C [15]. Ultimate crystal sizes corresponded to the crystal sizes produced at the lower synthesis temperature but yields were increased because of the higher temperature treatment. The yield of a the two-stage 60–100 °C procedure has further been improved by addition of methylene blue to the precursor suspension [16].

Temperatures higher than 100 °C have also been used to prepare nanozeolites of improved yield. Valtchev et al. have aged silicalite-1 and ZSM-5 precursor suspensions at room temperature for up to 60 days, which was followed by hydrothermal treatment at 230 °C for 2 h [17]. The product crystals were generally nanosized crystals with well-defined crystal facets but with broad particle size distributions. In addition, almost 100% silica conversion was achieved. Tatsumi et al. have pretreated silicalite-1 precursor suspensions at 80 °C for 24 h prior to hydrothermal treatment at 170 °C for 24 h to produce nanosized crystals [18]. Addition of L-glutamic acid resulted in further decrease of the crystal size, which effect was more pronounced for more diluted solutions.

The above examples undoubtedly indicate that complete silica conversion can only be achieved at high, >100 °C, temperatures. All precursor suspensions yielding nanosized silicalite-1 contain TPAOH in large excess, imposing a major barrier to industrial applications. TPAOH is unstable at high temperatures and decomposes, resulting in brownish color of the as made silicalite-1

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suspensions. Whereas there are numerous thermal analysis- studies on the decomposition of TPA cations from MFI-type precursors and crystals [19–26], these studies do not account for changes in the state of the excess TPA cations, which are not associated with the silicate species in the system. In all these works, samples were filtered/centrifuged prior to thermal analysis, thus leaving the excess SDA in the mother liquor. Hoffman type elimination followed by β -eliminations have been proposed to be the decomposition mechanism of TPA cations from the pores of MFI-type zeolites [19–23]. The TPA⁺ decomposition temperature has been found to strongly depend on the environment. For instance, the temperatures of max weight loss for pure TPAOH were 145 and 240 °C compared to a single temperature of 430 °C for TPA-silicalite-1 [19]. These results suggest that the decomposition mechanism of the excess TPA⁺ is probably similar to the decomposition mechanism of TPA cations occluded in the zeolite pores, but shifted to lower temperatures. TPA decomposition from silicalite-1 has also been found to depend on the specific conditions used during analysis, such as heating rate and gas atmosphere [23,27]. The objectives of the present study were to optimize the synthesis of nanosized silicalite-1 at high, ≥ 150 °C, temperatures in terms of crystal size and colloidal stability, and also to show that different synthesis procedures can influence the state of excess TPAOH molecules at the end of the high temperature hydrothermal treatment.

2. Experimental

Silicalite-1 clear precursor suspension was prepared from a mixture with the molar composition 9TPAOH: 25SiO₂: 480H₂O from tetrapropylammonium hydroxide (TPAOH, 1 M aqueous solution, Alfa Aesar), tetraethyl orthosilicate (98%, Aldrich) and distilled water [28]. The mixture was vigorously stirred for 1 h to hydrolyze the TEOS, followed by pretreatment for different periods using different pretreatment procedures. Initial pretreatment experiments were performed in an ultrasonic bath (Sonorex TK30, 50 kHz) for times of up to 9 h. No special measures were taken during the ultrasonic treatment to control the temperature of the ultrasonic bath, which raised to ca. 47 °C within 1 h. Further pretreatment experiments were performed in a water bath at 45 °C using similar pretreatment times. Last series of pretreatment experiments were performed in an oil bath under reflux. The pretreated synthesis solutions were transferred to PTFE-lined stainless steel autoclaves and hydrothermally treated at 150 °C for 19 h, or at 170 °C for 24 h. Reference zeolite samples were prepared similarly but without the pretreatment step. Finally, a silicalite-1 sample was prepared at 95 °C by transferring the precursor suspension to a polypropylene reactor followed by hydrothermal treatment in a conventional oven for 48 h. Pure TPAOH were also prepared in analogous experiments, with or without pretreatment. Some samples were crystallized in a microwave oven (Monowave 300, Anton Paar Ltd.) for 2 h at 150 °C. After the synthesis, the samples were purified by two-times centrifugation at 6000 rpm and redispersion in distilled water, and stored in distilled water.

The size and morphology of the samples was studied by scanning electron microscopy (SEM) using a JEOL 5600LV instrument. Droplets of the purified suspensions were dried on carbon tapes, which had been fastened to Al stubs, and coated with Au prior to analysis. Particle diameters and zeta potentials were determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS instrument with a 173° backscattering angle geometry. Thermogravimetric analysis (TGA) was performed with a TGA4000 instrument from Perkin Elmer. Samples were heated to 900 °C at a heating rate of 10 °C min⁻¹ under air.

3. Results and discussion

3.1. Preliminary optimization of the pretreatment procedure

Initial experiments were performed using an ultrasonic pretreatment for 5 and 9 h. As described in experimental, during pretreatment, the temperature of the ultrasonic bath gradually raised to ca. 47 °C. Microwave and conventional heating modes were used for the subsequent hydrothermal treatment at 150 °C. A decrease in the silicalite-1 size with an increase in the time of ultrasonic pretreatment was observed in both cases (Fig. 1). The decrease was more pronounced for the microwave synthesis (Fig. 1a–c) compared to conventional heating (Fig. 1e and f). To determine the effect of the temperature rise, experiments were performed using an ultrasonic treatment at 0 °C, by adding ice to the ultrasonic bath. It was found that in this case, the ultrasonic pretreatment had no effect on the size of silicalite-1 crystals (Fig. S1), indicating that the temperature rise was the main reason for the reduced crystal sizes observed in Fig. 1. This conclusion was confirmed by performing the pretreatment in a water bath at 45 °C. A similar degree of size reduction was observed for samples pretreated for the same periods of time in ultrasonic bath and in water bath (Fig. 1b and d). Ultrasound has been reported to increase the nucleation, particle growth and crystallization rates of silicalite-1 synthesized at 75 °C [29]. In this work, ultrasound was applied for short times during the initial stages of nucleation, which may be the reason for its insignificant effect on the final particle size. Thus, further optimization of the pretreatment procedure was carried out by preheating the samples without applying ultrasound. Oil bath and reflux conditions were used instead of water bath pretreatment when longer (≥ 24 h) pretreatment times were used. First, pretreatment experiments were performed at 45, 55 and 60 °C. The crystal size decreased with prolonging the pretreatment time and also with increasing the temperature (results not shown). Next, the influence of pretreatment time at 60 °C was studied. It was found that final particle sizes varied in the range 110–100 nm upon increasing the pretreatment time at 60 °C between 24 and 48 h, correspondingly. Samples prepared using a pretreatment for 24 h were then studied in detail and results will be presented in Section 3.3.

3.2. Hydrothermal treatment of pure TPAOH solutions

All samples after the hydrothermal treatment were milky suspensions. However, whereas the samples prepared by microwave heating and most of the samples prepared with pretreatment were whitish, the samples prepared by direct hydrothermal treatment at 150 and 170 °C in conventional oven were brownish. This suggested that the TPAOH decomposed at high temperatures and the decomposition was dependent on pretreatment. This effect was studied by applying different pretreatment procedures to pure 1 M TPAOH solutions followed by hydrothermal treatment at 150 or 180 °C for 19 h (Fig. 2). The samples prepared by direct treatment were brownish but the color intensity was more pronounced for the sample prepared at 150 °C (Fig. 2a and d). The samples prepared by pretreatment in water bath for 5 h were also brownish but there was a clear reduction in the colorization for the sample prepared at 180 °C (Fig. 2b and e). The samples prepared with ultrasonic pretreatment for 5 h were colorless at both temperatures (Fig. 2c and f). Another observation was that the samples prepared at 180 °C contained two immiscible liquid phases (Fig. 2d–g). These results indicated that the temperature of hydrothermal treatment and the pretreatment procedure had an effect on the decomposition products of TPAOH. Ultrasound is often used to degas liquids and remove microscopic bubbles. Vacuum filtration

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