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ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JULY 2009

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# Seed-Induced Crystallization of Nanosized Na-ZSM-5 Crystals

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ZSM-5 nanocrystals were synthesized from organic-template-free gel systems containing 0.1, 1.0, and 3.0 wt % of 80 nm silicalite-1 seeds. The syntheses were performed at 100, 120, 150, and 170 °C for periods of time ranging between 3 and 190 h. Physicochemical characteristics derived from XRD, NMR, TG/DTA, SEM/TEM, DLS, N<sub>2</sub> adsorption and chemical analyses of Na-ZSM-5 nanocrystals were compared with those of the nanosized tetrapropylammonium (TPA)-promoted counterpart. Crystalline yield and colloidal stability of ZSM-5 nanosized materials obtained under different conditions (seed content, crystallization temperature, and time) were also studied. Another issue of interest in the framework of this study was the effect of seed pretreatment (drying, calcination) on the characteristics of crystalline product. Thus, factors controlling seeded growth of nanosized zeolite particles were established and the mechanism of formation, including parameters governing the formation of single or aggregated crystals, revealed.

## Introduction

Zeolite nanocrystals have proven to be useful for a number of applications, where conventional micrometer-sized particles cannot be applied.<sup>1</sup> However, many synthesis-related issues remain to be addressed to make these materials readily available. In other words, the synthesis of zeolite nanocrystals with narrow particle size distribution that are able to provide a stable colloidal suspension is still a challenge. Consequently, different methods for production of nanosized zeolite crystals have been developed.<sup>2,3</sup> Nanocrystals with narrow particle size distribution are generally obtained from systems containing colloidal or sub-colloidal particles, which are usually denoted as “clear solutions”. The homogeneity of such systems is much higher with respect to the hydrogels conventionally employed in zeolite syntheses. Consequently, the simultaneity of the events in such systems leads to the formation of precursor gel particles and their transformation into uniform in size crystalline zeolitic material. To obtain such homogeneous starting systems, abundant amounts of tetraalkylammonium hydroxides and water are employed.<sup>4,5</sup> Another characteristic feature of such systems is the very low content of alkali cations. These factors, together with the careful choice of the reactants, allow the stabilization of a “clear” starting mixture, where only discrete gel particles are present.<sup>6–9</sup> Amongst different reactants, the input of the silica source on the evolution of the system is probably the most important.<sup>10</sup> Usually the lowest possible temperature for a particular zeolite is employed to favor the nucleation over the growth and thus smaller crystals to be obtained. At present, this is the commonly used approach for synthesis of zeolite nanocrystals.<sup>11–15</sup> However, the use of large amounts of tetraalkylammonium hydroxides and the low crystallization temperatures lead to low yield and thus to expensive products. Furthermore, the use of excessive amounts of expensive organic structure directing agents (SDA) is not appreciated from the environmental and economical points of view. In addition, the organic SDA requires high temperature calcination of the zeolite to open the porosity, which leads to aggregation of the individual particles and also

to volatile species which are far from being environmentally benign. A calcination procedure, where an organic polymer network is used as a temporary barrier during the high temperature treatment to prevent zeolite nanocrystal aggregation has been developed.<sup>16</sup> Nevertheless, alternative methods of synthesis that would avoid the above mentioned drawbacks will be highly appreciated.

Synthesis of discrete zeolite crystals from organic SDA-free systems is an interesting alternative since it circumvents the use of organic templates and consequent calcination step. For instance, nanosized zeolite L can be obtained without using an organic SDA.<sup>17</sup> Recently nanosized zeolite L has been produced in commercial scale by Clariant International Ltd., based on a procedure developed by Calzaferi et al.<sup>18</sup> Smaller crystals could be obtained by varying the gel composition and in particular the crystallization temperature. As a rule, a lower crystallization temperature leads to smaller particle sizes. Following this principle, Zhan et al. obtained organic template-free nanosized zeolite X at 60 °C.<sup>19</sup> Some of the undesired effects related to this approach are the decrease of the crystallization rate and sometimes the ultimate crystallinity. In addition to the temperature, the crystallization kinetics of any particular zeolite is affected by the alkalinity and the composition of the reaction mixture. In a series of studies, Valtchev et al. showed that nanosized LTA- and FAU-type zeolites could be obtained at room temperature by fine-tuning the gel composition.<sup>20–22</sup> The syntheses were performed for reasonable periods of time because of the very reactive initial systems employed. This approach, however, is limited to the synthesis of low silica zeolites crystallizing from highly reactive gels comprising alkali and alkali-earth cations.

Syntheses of zeolite nanocrystals within an inert matrix providing a steric hindered space for crystal growth have also been developed. The first example of such a synthesis was reported by Madsen and Jacobsen for the preparation of nanosized ZSM-5 crystals.<sup>23</sup> The procedure consisted of incipient wetness impregnation of mesoporous carbon black with a zeolite precursor that is consequently subjected to autoclave treatment in saturated steam. Disadvantages of the method are related with the requirements imposed to the matrix, that is, inertness and stability under the experimental conditions and

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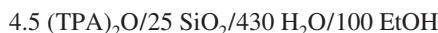
sharp mesopore size distribution to yield uniform zeolite crystals. Another approach to zeolite nanocrystals preparation that could be considered as confined-media synthesis was also developed. Again, low silica organic template-free zeolites were synthesized using starch<sup>24</sup> and thermo-reversible polymer hydrogel<sup>25</sup> as a space limit agent. Lew et al. reported better yield for silicalite-1 nanocrystals by addition of methylene blue in starting gels.<sup>26</sup>

An alternative approach that could address the requirements for environmentally benign and economically acceptable synthesis of nanozeolites is the seeded crystallization. This method is commonly used in the crystallization of conventional zeolite crystals to (i) increase the crystallization rate, (ii) suppress the formation of undesired phases, (iii) control the particle size, and (iv) enable the intergrowth of zeolite films on functional surfaces.<sup>27–33</sup> Seeded crystallization of nanosized ZSM-5 particles has been reported by Reding et al.<sup>34</sup> However, in addition to a large amount of seeds (>10 wt %) an organic template (tetrapropylammonium) has also been employed in these syntheses. The work of Chen et al.,<sup>35</sup> who have studied the influence of diverse synthesis parameters on the crystallization of ZSM-5 nanoparticles, should also be acknowledged. Although, the latter study does not discuss the effect of seeds on ZSM-5 formation, it provides a useful background for the organic template-free synthesis of ZSM-5.

The present study reports on the synthesis of nanosized ZSM-5 crystals from organic-template-free systems. Crystal growth kinetics, crystalline yield, and physicochemical properties of zeolite nanoparticles as a function of the seed concentration and synthesis temperature are addressed.

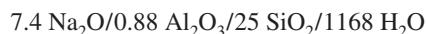
## Experimental Section

**Preparation of the Seed Suspension.** The reactants used in the synthesis were tetraethylorthosilicate (TEOS, Merck), tetrapropylammonium (TPA) hydroxide (20 % in water, Merck) and distilled water. After mixing of the reactants, the solution was allowed to hydrolyze at room temperature for 14 hours and then treated hydrothermally at 90°C for 24 h. The starting composition of the clear solution used for seeds synthesis was

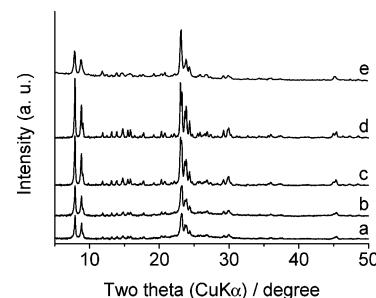


The presence of ethanol (EtOH) in this composition is a consequence of the use of TEOS as a silica source. After the synthesis, the zeolite suspension was purified by four series of high-speed centrifugation (20 000 rpm, 1 h), decanting, and re-dispersion in distilled water. The zeolite solid content in the seeding suspensions was adjusted to 0.1, 1.0, and 3.0 wt. % and then the pH to 9.5 by adding 0.1 M NH<sub>3</sub>.

**Seeded Synthesis of Nanosized Na-ZSM-5.** Precursor gels containing 0.1, 1.0, and 3.0 wt. % seeds in respect to silica content were prepared. A solution of sodium silicate (VWR Prolabo, 10 % NaOH and 27 % SiO<sub>2</sub>), distilled water, and seed suspension was stirred for 20 min. A second solution of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•18H<sub>2</sub>O (Rectapur Prolabo) in water was added into the first one under vigorous stirring. The composition of the initial mixture was



The hydrothermal treatment was performed at 100, 120, 150, and 170 °C. After the crystallization, the solid was recovered in a series of four steps consisting of high speed centrifugation, removal of the mother liquor, and re-dispersion in distilled water.



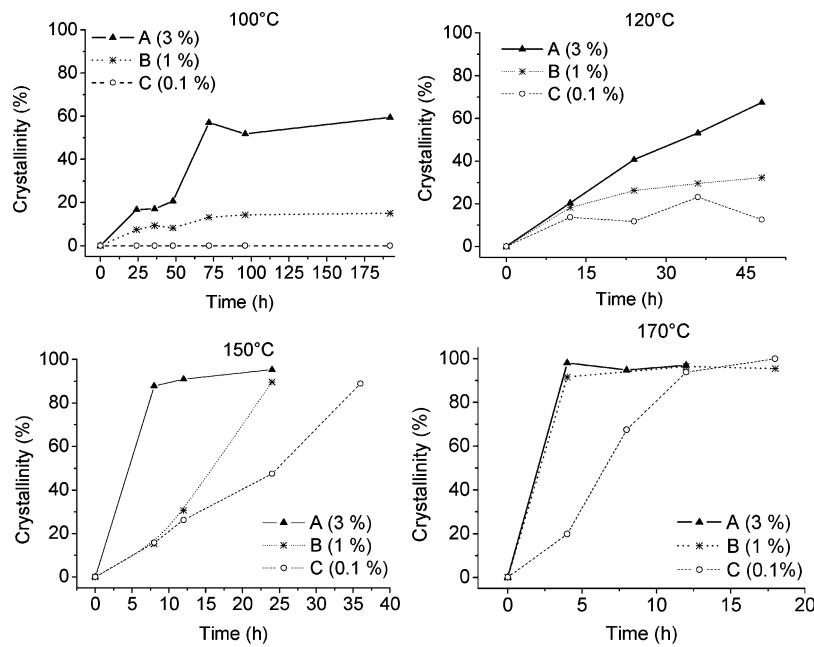
**Figure 1.** X-ray diffractograms of representative samples with the highest crystallinity for each synthesis temperature obtained using 3 wt % seeds at 100 °C, 8 days (a), 120 °C, 48 h (b), 150 °C, 36 h (c), and 170 °C, 18 h (d) and nanosized silicalite-1 crystals employed as seeds (e).

A reference sample (see Supporting Information) was prepared according to the procedure published by Van Grieken et al.<sup>36</sup> The initial gel with composition 10.7 (TPA)<sub>2</sub>O/1.0 Al<sub>2</sub>O<sub>3</sub>/60 SiO<sub>2</sub>/650 H<sub>2</sub>O was subjected to hydrothermal treatment at 170°C for 20 h. The sample was purified according to the above procedure.

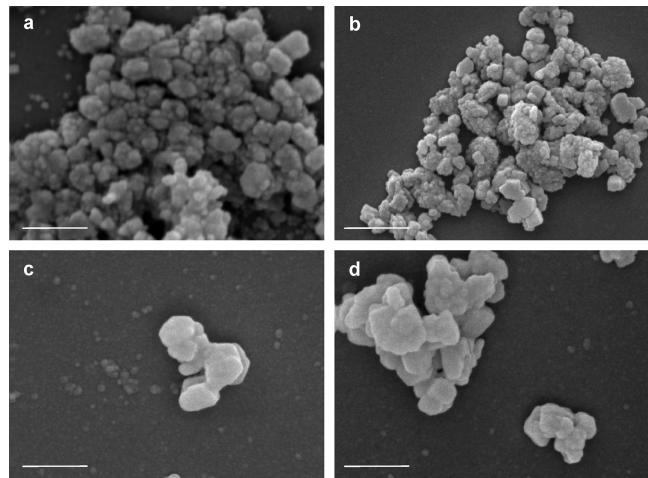
**Characterization.** The obtained materials were studied by X-ray diffraction (XRD) using a PANalytical X'Pert Pro diffractometer in Debye–Scherrer geometry equipped with a linear position-sensitive detector (6° in 2θ) and employing Ge-monochromated Cu K<sub>α1</sub> radiation. Electron micrographs were taken on a Philips XL30 FEG scanning electron microscope (SEM). The TEM images and SAED patterns were taken with a JEOL JEM 2011 microscope operating at 200 kV (Cs = 1.0 mm). The <sup>27</sup>Al MAS NMR spectra were recorded on a Bruker Avance<sup>II</sup> 400 FT spectrometer ( $\omega_0$  = 12000 MHz, MAS  $\pi/2$  pulse of 2.08  $\mu$ s with a recycling time of 0.5 s). The <sup>29</sup>Si MAS NMR spectra were recorded on a Bruker Avance<sup>II</sup> 400 FT spectrometer at 79.495 MHz with a pulse length of 2.08  $\mu$ s and a spinning rate of 4 kHz. Nitrogen adsorption measurements were carried out on a Micromeritics ASAP 2040 surface area analyzer. The samples were analyzed after degassing at 300°C. The combined TG/DTA analysis of the samples was performed with a Setaram TG-ATD LABSYS thermal analyzer at a heating rate of 5° min<sup>-1</sup> in an atmosphere containing 80 % N<sub>2</sub> and 20 % O<sub>2</sub>. The elemental analyses of the core crystals were performed on an X-ray fluorescence spectrometer MagiX (Philips).

## Results

In the present study, the chemical composition of the initial system was optimized using 0.1 wt % seeds. The preliminary study involved the variation of the ratio between the components of the initial gel until a material with a high crystallinity was obtained for relatively short crystallization time. The hydrothermal treatment (150 °C for 48 h) of the initial gel without adding seeds resulted in the formation of a mixture of MFI- and MOR-type material. Thus, the use of seeds was deemed necessary not only to decrease the crystal size but also to obtain pure MFI-type material in the system under investigation. Furthermore, the performed set of experiments revealed the effect of different parameters on the formation of ZSM-5 nanocrystals. The evolution of crystallinity of the samples as a function of the seed content and crystallization temperature was followed by XRD analysis. Representative X-ray diffractograms of samples with the highest crystallinity obtained at different temperatures are presented in Figure 1. Crystallization curves for all syntheses are depicted in Figure 2. The obtained data show that both the seed content and the crystallization temper-



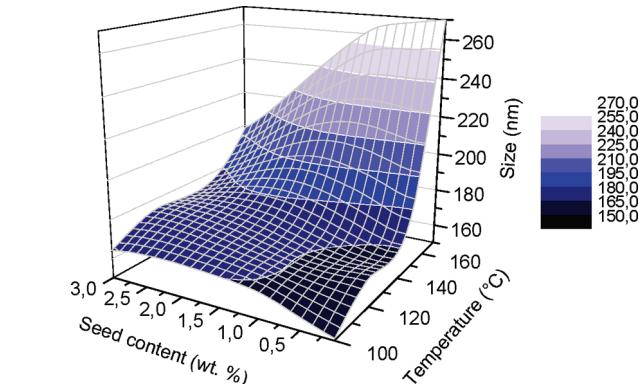
**Figure 2.** Crystal growth kinetics of the materials synthesized at 100 (a), 120 (b), 150 (c), and 170 °C (d) with 0.1, 1.0, and 3.0 wt % seeds. The lines are a guide to the eye.



**Figure 3.** Representative SEM micrographs of the samples synthesized at 100 °C, 8d (a), 120 °C, 48 h (b), 150 °C, 36 h (c) and 170 °C, 18 h (d). Scale bar 200 nm.

ature strongly influenced the ultimate crystallinity of nanosized ZSM-5. The highest crystallinity reached at different temperatures was as follows: 170 °C, 100%; 150 °C, 93%; 120 °C, 68%; 100 °C, 59%. Besides higher crystallinity, much faster growth kinetics was observed at higher temperatures (170 and 150 °C). The seed content also influenced the growth kinetics strongly. For instance, at 170 °C, only 3 h of hydrothermal treatment were necessary to obtain fully crystalline ZSM-5 material when 3 wt % seeds was used, while the decrease of the seed content to 0.1 wt % resulted in several times longer crystallization (18 h). It should be mentioned that at lower temperatures (100 and 120 °C) the crystallinity was below 100% even with high seed content (3 wt %) and after a substantial prolongation of the synthesis time (Figure 2).

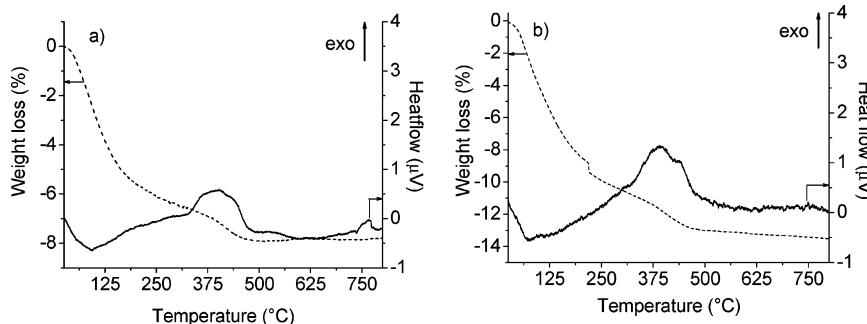
SEM inspection of the samples showed products with fairly different size and morphology. The size of the individual crystals obtained at different temperatures varies from several tenths to several hundred nanometers (Figure 3). As mentioned in the Introduction, the crystallization temperature strongly affects the



**Figure 4.** Diagram representing the mean particle size (number weighted) as a function of the synthesis temperature and seed content.

crystal size of zeolites. It seems this relation is also valid for the seeded zeolite synthesis. For instance, for 3 wt % seeded gels, nanocrystallites with size range of 30–70 nm were observed in samples obtained at 100 and 120 °C, while the main fraction of crystals obtained at 150 °C was between 130 and 160 nm, and crystals larger than 200 nm were obtained at 170 °C. Much larger (400–700 nm) crystals were obtained at 170 °C when the synthesis time was extended to 24 h. The employed amount of seeds did not have an important effect on the size of the main crystalline fraction but on the degree of agglomeration, which was confirmed by DLS measurements (Figure 4). It should be mentioned that abundant intergrowth was observed in most of the samples, which makes difficult to evaluate the dominant population of nanoparticles by SEM.

DLS analysis was employed to evaluate the average particle size in the obtained colloidal crystalline suspensions. Prior to analysis, the colloidal suspensions were kept 10 days at room temperature to sediment the larger particles. A drop of the colloidal suspensions was diluted with double distilled water and subjected to analysis. The DLS data were found to be in a good agreement with the SEM observations, that is, the size of the ZSM-5 particles was a function of the increase in temperature. Particle size analysis revealed also a relationship that was

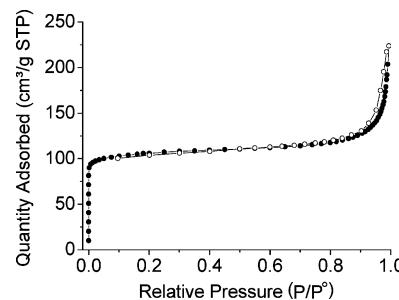


**Figure 5.** TG/DTA analyses of ZSM-5 nanocrystals obtained at 170 °C for 18 h (a) and at 120 °C for 45 h (b). Weight loss: dotted line. Thermal response: solid line.

not so evident by SEM inspection of the samples seeded with different amounts of nanocrystals. Namely, the increase of the seed content led to a greater amount of smaller particles (Figure 4). Furthermore, the mass of zeolite particles in colloidal form and the sediment were evaluated. The mass of sedimented material at different temperature was 23, 29, 36, and 47 wt % for 100, 120, 150, and 170 °C, respectively. It should be mentioned, however, that no difference was observed between the size of the zeolite crystals floating in the suspension and those in the sedimented aggregates. It is also important to notice that the content of non-colloidal particles increases with crystallization temperature and almost a half of the product obtained at 170 °C did not show colloidal stability.

TPA-containing silicalite-1 seeds were employed in all synthesis of ZSM-5. Therefore, it is essential to evaluate the amount of the organic structure-directing agent occluded in the ZSM-5 nanocrystals. TG/DTA analysis showed that final highly crystalline materials comprise a negligible amount of template. The small exothermic peak in the temperature range of 350–450 °C corresponds to a weight loss of about 0.4 wt %, which was observed in the sample synthesized with 3 wt % seeds at 170 °C (Figure 5a). The template content in ZSM-5 nanocrystals is negligible in respect to the one (11.2 wt %) found in the reference sample. The weight loss (~6 wt %) in the temperature range of 50–200°C was attributed to water release. It should be mentioned that this is a relatively high water content for a MFI-type material. Even higher water content was found in the samples obtained at lower temperatures, for instance, the sample synthesized at 120 °C comprised about 10 wt % water (Figure 5b). The desorption range corresponding to the endothermic peak was much larger (50–350 °C) for this sample in respect to one synthesized at 170 °C. The overlapping of the areas corresponding to the water and template release made it difficult to estimate correctly the template incorporated into ZSM-5 nanoparticles synthesized at 120 °C. Consequently, it was not possible to establish a correlation between the seed content and the amount of TPA transferred from the seeds into the ZSM-5 nanocrystals. As mentioned before, a particularity of the sample synthesized at 120 °C was the broader temperature range corresponding to water release. In general, loosely bound water in zeolite channels is desorbed in a much narrower temperature range. The higher temperature shift of the peak suggests the presence of some amorphous material comprising strongly bound water.

Type I adsorption/desorption isotherms typical of microporous materials were observed for all samples (Figure 6). The steep uptake at low relative pressure was followed by nearly horizontal adsorption and desorption branches. A second uptake at high relative pressure was also observed for all samples. The upward turn with a hysteresis loop is indicative of the generated



**Figure 6.** Nitrogen adsorption/desorption isotherms of the sample synthesized at 150 °C for 24 h.

intercrystalline mesoporosity, which is not surprising having in mind the abundant aggregation of the nanocrystallites. BET calculation showed specific surface areas ranging between 330 and 380 m<sup>2</sup> g<sup>-1</sup> for the samples synthesized at different temperatures, which is a little below the one expected for a highly crystalline MFI-type material (~400 m<sup>2</sup> g<sup>-1</sup>). The micropore volume is close but still below the one calculated for the reference sample (Table 1) suggesting that the sample contains small amount of low surface area material. The adsorption data revealed also that the micropore volume is a function of the crystallization temperature. Thus the synthesis performed at low temperatures (100 and 120 °C) provided materials with lower micropore volume and larger external surface area (Table 1).

Chemical analyses of nanozeolite products showed extremely low Si/Al ratio for MFI-type material (~10). Interestingly, the chemical compositions of the highly crystal materials obtained at 170 °C and 150 °C do not differ from those containing some amount of amorphous material (120 °C and 100 °C). For comparison, the lowest Si/Al ratio of ZSM-5 crystals published in the open literature is 10.3.<sup>37</sup> The observed further decrease in Si/Al ratio is a consequence of using solely sodium as structure directing agent. This result is in conformity to the negligible amount of TPA and high water content found by TG analysis.

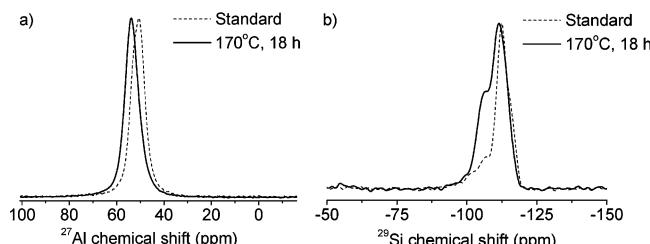
The question that arises upon regarding the extremely high aluminum content of the nanosized ZSM-5 is whether all aluminum was incorporated in the framework. <sup>27</sup>Al MAS NMR analysis was performed on samples with the highest crystallinity at a given temperature (Figure 7a). All spectra showed a peak at 55 ppm representative of a tetrahedral environment for the aluminum, independent from crystallization temperature or seed content. The absence of a peak at 0 ppm unambiguously proofs that all aluminum is incorporated in the zeolite framework.

<sup>29</sup>Si MAS NMR of the reference ZSM-5 sample and materials obtained at 170°C are shown in Figure 7b. It is apparent that

**Table 1.** Physicochemical Characteristics of ZSM-5 Samples with the Highest Crystallinity Obtained with 3 wt % Seeds at Different Crystallization Temperatures

synthesis temperature, °C	XRD crystallinity, %	framework Si/Al ratio	crystalline yield <sup>a</sup> , %	micropore volume, cm <sup>3</sup> /g	external surface area, m <sup>2</sup> /g
90 <sup>b</sup>	100	∞		0.17	102
100	59	10.2	81	0.07	61
120	68	10.1	83	0.08	71
150	95	9.6	89	0.12	53
170	100	10.0	92	0.13	39

<sup>a</sup> The yield is calculated on the basis of silica conversion. <sup>b</sup> Standard sample used for seeding.



**Figure 7.**  $^{27}\text{Al}$  MAS (a) and  $^{29}\text{Si}$  MAS (b) decoupled NMR spectra of sample synthesized at 170°C for 18 h in comparison with the silicalite-1 seeds.

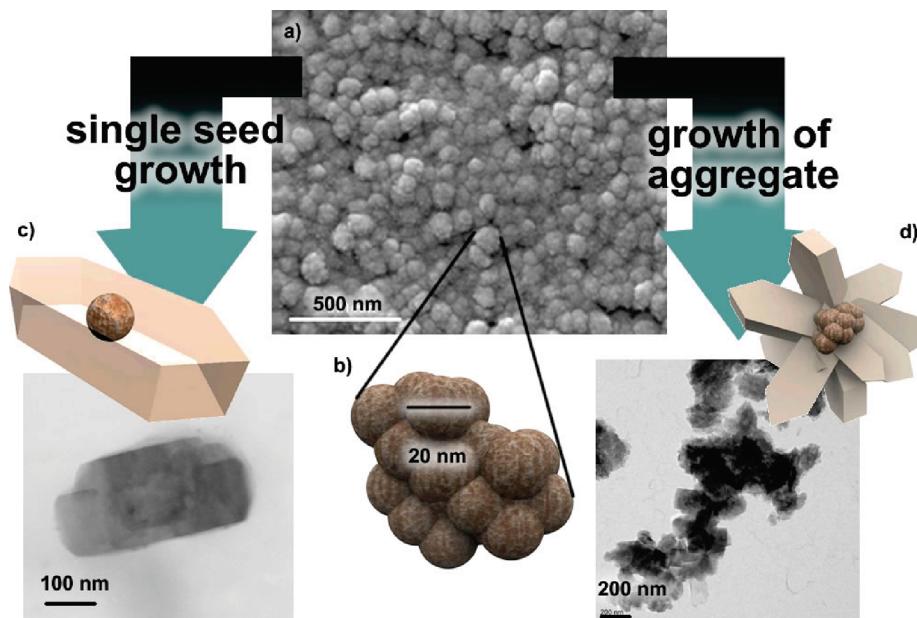
the higher aluminum content in seeded ZSM-5 syntheses leads to a significant broadening of the Q<sup>4</sup> bands ( $-111.82$  ppm). Higher aluminum content is also evident by more intense Q<sup>3</sup> peak ( $-106.34$  ppm) in template-free samples. In addition, a small Q<sup>2</sup> band revealing the presence of some amorphous material in ZSM-5 samples synthesized at 120°C and 100°C was found (not shown here). These data are in a good agreement with the other analyses of the products, in particular with the TG and XRD studies.

## Discussion

Seeding is a widely used approach in the large-scale production of zeolites. Nevertheless, the exact mechanism that promotes zeolite crystallization in a seeded system has not been fully understood.<sup>38</sup> It is still not clear which are the active species promoting the growth in a seeded zeolite yielding system. There is no doubt, however, that seeds smaller in size increase the rate of crystallization in respect to larger ones. This effect is caused by the larger cumulative external surface area of the smaller particles. Thus, smaller or nanocrystals are more appropriate for seeding of synthesis gels. Another important issue related to the seeded zeolite synthesis is the uniform distribution of the particles within the amorphous precursors. Again, the nanoparticles in the form of colloidal suspension offer the advantage of a uniform distribution into the synthesis gel. Thus, colloids comprising the smallest possible seeds seem to be the best choice for the synthesis of nanosized zeolitic particles with a narrow size distribution since in a closed nutrient pool the ultimate crystal size depends on the number of viable nuclei that grow into crystals. It is known that, because of specific conditions used in the synthesis of nanocrystals, they often form aggregates built of much smaller crystalline domains. If the hypothesis that nanoentities from larger crystals promote the crystallization in seeded systems is correct,<sup>39</sup> then the nanocrystals are particularly appropriate for seeding zeolite-yielding gels. According to the DLS analysis the seed crystals have a narrow particle size distribution with an average size of about 80 nm. The particle size was confirmed by SEM characterization as well. However, the latter shows that the particles are aggregates consisting of much smaller crystals (Figure 8a). These very small (10–30 nm) crystals comprise high surface

energy faces that readily continue their growth under appropriate conditions. On the other hand, these particles are already crystalline containing at least 5 unit cells, which makes them sufficiently stable in a system different from the one they used to grow. The efficiency of these nanocrystals as seeds was proven by the rapid crystal growth kinetics of ZSM-5 and by the formation of nanosized crystals. The presence of both, single isolated crystals and complex aggregates, suggests that the growth process is promoted by two types of seed: (i) a single isolated bred released from the aggregates and (ii) complex aggregates comprising large number of single bred-nuclei. The TEM examination of the crystalline products shows that a great part of material is in the form of random aggregates. A much diluted initial system is employed to reduce the intergrowth for avoiding the development of closely situated crystallites. Nevertheless, abundant intergrowth was observed in all samples and the number of isolated well-shaped crystals was limited. The most likely origin for the abundant intergrowth is the presence of seeds, which are governing the growth in the system. The drawing in Figure 8, supported by TEM images, represents the two types of seeds. The domination of the aggregates in the product is in good agreement with the above suggestion, that is, the mass of aggregated nanoparticles growing into crystals is much higher than that of single bred nuclei. The low number of single isolated crystals can be explained by either limited breeding or by the released bred nuclei staying in close proximity of parent aggregate and thus their development into crystals results in complex aggregates. Therefore, the formation of nanoparticles with narrow particle size distribution cannot be expected if the growth in the system is promoted by complex aggregates, even being with nanometric size.

For the system under investigation, both the seed content and the crystallization temperature showed a very pronounced effect on the formation of nanocrystals. These two parameters controlled the ultimate crystallinity and the kinetics of crystal growth. Interestingly, the effect of one of these variables could be partially compensated by the other. For a given temperature, the seed content determines the crystal growth kinetics and ultimate crystallinity. Similarly, for a given seed content, the kinetics of formation and the crystallinity of the zeolite samples depend on the crystallization temperature. Thus, different combinations of seed content and crystallization temperature could be employed in order to achieve similar particle size or crystallinity. On the other hand, the ultimate crystallinity of the solids is not equally influenced at lower and higher temperatures, that is, maximum (100 %) crystallinity is difficult to be achieved at lower temperatures (100 and 120 °C). A possible explanation for the lower conversion could be the slow growth kinetics. Namely, the slow transformation of precursor aluminosilicates allows the formation of other stable species which are more difficult to transform into zeolite phase. The extension of the crystallization time did not result in products with higher crystallinity. Even after 9 days

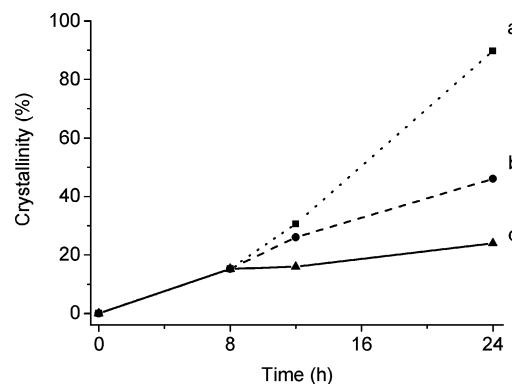


**Figure 8.** SEM micrograph of silicalite-1 nanocrystals used for seeding of initial gels (a), a sketch of a seed aggregate (b), and the result of the secondary growth of a monocrystalline particle and a polycrystalline aggregate exemplified by TEM images (c and d, respectively).

hydrothermal treatment at 100 °C, the product was not fully crystalline. It should be taken into consideration that Na-ZSM-5 is much less stable under hydrothermal conditions than the TPA-containing counterpart. Hence, its transformation into more stable aluminosilicate phases can be expected if the hydrothermal treatment is substantially extended. Thus, the modification of the gel composition is probably the most appropriate solution in order to reach higher crystallinity at lower crystallization temperature. The latter, however, is out of the scope of the present study.

Although larger nanocrystals with broader particle size distribution in respect to the organic-template-rich syntheses were obtained, the product still remains in the nanometric range. The impact of the particle size on the colloidal properties of the material was less pronounced than that of the intergrowth and the aggregation of the crystals. Namely, large complex aggregates built of very small individual particles were found in sedimented material. The mass of large particles in some syntheses was close to 50 % (Table 1). Nevertheless, the obtained colloidal fraction was comparable in mass to organic template promoted crystallization. This phenomenon is caused by the relatively high yield in seeded systems (Table 1). Thus, the seeded approach is an interesting alternative to organic-templated crystallization for the synthesis of nanozeolites.

To evaluate the effect of pretreatment of the seeds on the crystal growth of the zeolite, additional experiments were performed. Silicalite-1 nanocrystals, purified and freeze-dried, were employed as seeding materials for studying the kinetics of crystal growth of ZSM-5 at 150 °C. In a separate experiment, seeds calcined at 500°C for 16 h were used for seeding, and the synthesis was again performed at 150 °C. The results of this study are presented at Figure 9. As can be seen, the efficiency of freeze dried and calcined seeds is lower with respect to purified suspensions of nanoseeds used in this study. For the similar duration (24 h), well-dispersed seeds introduced as colloidal suspension provided fully crystalline material. In contrast, the crystallization induced by freeze dried seeds reached only 40% crystallinity. Even lower crystallinity was



**Figure 9.** Crystallization curves obtained at 150 °C using 1 wt % seeds: suspension (a), freeze-dried (b), and freeze dried and calcined (c). The lines are a guide to the eye.

calculated for the sample obtained with calcined seeds. This data unambiguously shows the importance of an intimate mixing of the seeds with the initial gel, which is influenced by post-synthesis treatment methods. On the other hand, the stability and reactivity of the calcined seeds is strongly influenced by the calcination. The effects of the high-temperature treatment are possibly related to the passivation of the external surface of the crystals, irreversible aggregation, and the elimination of TPA cations that might stabilize the MFI-type of seeds.

A characteristic feature of the seeded ZSM-5 nanocrystals is the low Si/Al ratio of the framework. This is a consequence of the exclusively employment of sodium as structure directing agent and low Si/Al ratio of the initial gel. The use of all-silica (silicalite-1) seeds did not influence the chemical composition of the final product. Nanocrystals with Si/Al ratio of about 10 were obtained, which is on par with the lowest obtained in the presence of TPA up to now (~10.3).<sup>40</sup> It is worth mentioning that all aluminum is incorporated in the framework according to the <sup>27</sup>Al NMR analysis. Thus, a higher amount of acid sites and interesting catalytic performance

of the nanocrystals issued from the organic template-free synthesis might be expected.

## Conclusions

The present study shows that zeolite nanocrystals can be synthesized by seeding of an organic-template-free initial gel. However, the level of crystal aggregation is much higher in respect to the syntheses performed from a clear solution rich with tetraalkylammonium hydroxides. The high aggregation level is most probably the result of the nanoseeds, which are in turn polycrystalline aggregates built of much smaller crystallites. The secondary growth of closely situated nanocrystallites leads to the formation of complex aggregates larger in size in respect to the seeding particles. Consequently a part of the product does not behave as colloid, although the size of the individual crystals lies in the nanometric range. The remaining part (over 50%) possesses all characteristic features of colloidal zeolite synthesized in organic template rich systems and could be further used for colloid-related applications.

Seeded syntheses of zeolite nanocrystals offer an alternative to the templated ones. First of all, the absence of an organic structure directing agent makes the synthesis environmentally benign. The product obtained does not require calcination, and thus, the post-synthesis aggregation between zeolite particles is avoided. The latter is a serious drawback in a number of applications involving the use of colloidal zeolite suspensions. Although methods for decreasing the level of aggregation have been reported,<sup>16,39</sup> the approach described in the present study is more attractive for its simplicity and environmentally friendly character.

The possibility to synthesize zeolite nanoparticles by seeding of the initial gel was exemplified by the synthesis of one of the most widely used zeolites. In addition, the results of the investigation gives further outline for the production of other zeolite structure types in the form of nanoparticles without using organic structure directing agents.

## Acknowledgment

The authors gratefully acknowledge funding from French-Croatia (COGITO) and French-Spanish (PICASSO) bilateral programs, PNANO ANR and support from SOILCY 6th FP EC.

**Supporting Information Available:** XRD pattern of reference sample, diffractograms of the ZSM-5 materials obtained with 1 wt % seeds introduced in colloidal, freeze-dried, and calcined form, and <sup>29</sup>Si MAS NMR spectra of samples synthesized with 0.1 and 1.0 wt % seeds at 170 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review November 12, 2008

Revised manuscript received June 4, 2009

Accepted June 4, 2009

IE8017252