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ARTICLE

Low Temperature Synthesis of Nanosized NaY Zeolite Crystals from Organic-Free Gel by Using Supported Seeds.

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Zeolite crystals having faujasite-type (FAU) topology and particle size distribution in the nanometer range have been successfully prepared by a room temperature, short duration synthesis, in absence of organic structure directing agents (SDAs). The use of NaX seeds anchored on α-Al_2O_3 tubular supports, jointly to the optimal composition of the precursor gel system, allowed to control the zeolite nanocrystals size and phase purity, and to reach a high degree of conversion of the precursor gel system into a nanocrystalline material at near ambient conditions. The X-ray diffraction (XRD) pattern collected on the samples confirmed the structural features reported for a FAU(Y) phase. The particle size of the zeolite nanocrystals was strongly dependent on the amount of seeds anchored on the supports. The mean particle size of different samples was estimated by SEM and measured by DLS, with similar results falling in the range of 35-60 nm. SEM observations also revealed that aggregates of primary crystals are present, whose size is still in the nanometer range. The synthesis approach described in the present study effectively addresses some significant issues related to the classical seeded syntheses and offers good opportunities for industrial applications. In particular, this novel synthetic route allows to avoid tedious purification procedures and effectively reduces the cost of the zeolite synthesis.

1. Introduction.

Over the past decades, crystalline zeolites and zeolite-like materials have shown enormous potential for several industrial-significant applications as diverse as catalysis, adsorption, ion exchange and separation.[1-8] The regular and flexible microporous structure of zeolites, their elevated surface area and superior chemical, thermal and mechanical stability are among the major reasons for their utilization in many traditional and emerging fields.

Recently, zeolites with particle size in the nanometer range have been subject of intense research, as reflected in a number of excellent reviews appeared over the last years.[9-11] The scaling down of the particles size causes dramatic changes in term of properties and performances of nanozeolites with respect to conventional zeolite materials. Nanozeolites valuably combine large external surface area, tuneable surface (charge, acidity and hydrophilic/hydrophobic) properties, flexible interactions with guest molecules and high loading capacity. The decrease of the particle size also results into an enhanced accessibility to the active microporous volume and an important reduction of the intracrystalline diffusion paths, providing an effective way for mitigating the adverse effects of mass transport limitation which occur within the zeolite pores. These features are particularly advantageous for many traditional applications of zeolites, like catalysis and adsorption.[12-15] In addition, the possibility of assembling nanozeolites into thin layers or hierarchically structured materials with unique properties opens up the opportunity for novel applications, including the construction of reactive membranes, selective chemical sensors and versatile nano-structures and nano-devices for opto-electronic and biomedical technologies.[16-23]

At present, different strategies are available for preparing nanozeolites. Commonly, they are synthesized under hydrothermal condition from homogeneous clear solutions or gels containing large amounts of organic SDAs.[24-27] Nevertheless, this approach can be hardly scaled up, due to the evident industrial and environmental concerns resulting from i) the use of expensive and toxic organic templates, ii) the need for high temperature post-synthesis treatments and challenging purification procedures and iii) the typically low crystalline yields.[28, 29]

To circumvent these obstacles, renewed efforts have been recently devoted to the synthesis of nanozeolites in absence of SDAs.[30] Typically, an alkali metal rich hydrogel is used as starting system and the crystallization process is carried out under mild conditions to favour nucleation over crystal growth and to reduce particle intergrowth. Several pure nanosized crystals have been successfully prepared by this method in high crystalline yield.[31-36] Nevertheless, the reproducibility of the process is extremely dependent on the synthesis conditions,

which have a major role in determining the ultimate phase purity, size and morphology of the synthesized crystals. Temperature and crystallization time, as well as the starting gel composition (chemical composition of the precursor solution, nature of the aluminium and silicon sources, choice of the mineraliser agent, ect.) need to be carefully controlled for favouring the abundant and uniform nucleation of the desired zeolite phase in the precursor system.

A more generalized approach to prepare nanozeolites in absence of organic SDAs exploits the seeding of the reaction mixture.[37-39] The seeded-assisted approach benefits from shorter crystallization time and assures a higher control over the particle size and the ultimate framework topology. Besides, it opens the possibility to access to a larger variety of zeolite structures and to reach higher silica contents. However, poorly crystalline products are usually obtained at low temperatures (<100°C), even when higher seed contents and prolonged synthesis times are employed. In addition, severe aggregation is usually observed and several purification steps are required for separating the micron-sized particles from the synthesized nanozeolites.

Within this context, we have recently reported a sort of "modified seeded-assisted" approach for the organic-free hydrothermal synthesis of NaY nanocrystals, a very commonly studied and industrial important zeolite.[40] The method implies the use of a supported FAU membrane to promote and direct crystallization. This approach allows to avoid challenging purification procedures, as the membrane can be readily removed at the end of the reaction.

With the aim of opening to industrial prospects and getting more convenient routes for large-scale production, we designed an alternative strategy to the conventional seeded-assisted synthesis of nanosized NaY crystals. Micron-sized NaX seeds anchored on α-Al$_2$O$_3$ tubular supports have been used to promote crystallization of NaY nanocrystals from an organic-free, hydroxyl-rich precursor system, in a short-time duration reaction conducted at near ambient condition. With respect to a traditional seeded synthesis, the method still has the advantage of avoiding tedious purification procedures, since the seeded support can be easily removed from the reaction batch. Moreover, the cost of the nanozeolite synthesis has been lowered, as the supported seeds can be re-used for successive syntheses. Finally, this strategy allows to reach a substantial reduction of the synthesis time and a high conversion of the initial system into pure zeolite nanocrystals at near room conditions, without using any organic SDAs or solvents.

2. Experimental.

2.1 Preparation of the Seeded Supports.

Different seed suspensions were prepared and used to study the influence of the amount of supported seeds on the ultimate particle size and crystalline yield of the synthesized nanocrystals. 25 (i), 50 (ii) or 100 mg (iii) of NaX zeolite crystals (Sigma-Aldrich) having a mean crystals size of about 2

µm and a Si/Al ratio of 1.5 were dispersed in 10 ml of distilled water and the suspension was vigorously stirred for 1h.

Porous α-Al$_2$O$_3$ asymmetric tubes were used as supports (IKTS, I.D. = 7 mm, O.D. = 10 mm, length = 100 mm, dpore = 100 or 70 nm). The supports were boiled in a NaOH solution 0.1 M for 1 hour, in order to activate the pendant hydroxyl groups on the support surface. The seeding procedure was carried out by carefully coating the suspension on the support surface to achieve a uniform deposition of the seeds on the whole inner surface area. The amount of seeds (wt/wt %) layered onto the support surface was ca. 2.5 (i), 5 (ii) and 10% (iii) with respect to the starting amount of SiO$_2$ used in the successive synthesis of the zeolite nanocrystals.

The seeded support was then placed into a Teflon-lined autoclave and a thermal treatment was performed in a pre-heated furnace at 160°C for 6 hours without any solvent, to engender the condensation reaction between the seeds and the support.

2.2 Synthesis conditions.

A synthesis gel with the following starting molar composition: 4.3SiO$_2$:1Al$_2$O$_3$:15.2NaOH:321.4H$_2$O was used for the synthesis of the nanosized zeolites. All the reagents used for preparing the solution were purchased from commercial sources and used without further purification: Sodium Aluminate (Carlo Erba Reagenti, 53–55% Al$_2$O$_3$), Sodium Silicate Solution (Aldrich, NaOH 14 wt.% and SiO$_2$ 27 wt.%), Sodium Hydroxide (NaOH pellets, 97%, Carlo Erba Reagenti). The reaction gel system was prepared at ambient temperature, by gently adding a clear water solution containing the sodium aluminate and the sodium hydroxide reagents to the sodium silicate solution in a LDPE bottle under continuous stirring. A clear suspension was obtained, which turned into a dense milky gel in few minutes. The synthesis of the zeolite nanocrystals was carried out under static condition, by pouring the synthesis solution in a cylindrical vial containing the seeded support (wrapped with Teflon tape in order to avoid crystallization on the outer surface). The vial was horizontally placed in a conventional oven at 30°C for 24 hours. A reference sample was prepared in the same synthesis conditions without the seeded support.

After 24 hours, the seeded supports were removed from the reaction batches. The reaction products were recovered and separated from the non-reacted mother liquors by centrifugation, then dried overnight in a conventional oven at 80°C. The relative crystalline yield (wt/wt %) of the reactions, defined as the amount of obtained zeolite crystals divided by the starting amount of SiO$_2$, was ca. 42% (i), 47%(ii) and 51% (iii).

2.3 Characterizations.

The morphology of the zeolite particles prepared in this work was investigated by using a Cambridge Zeiss LEO 400 scanning electron microscope (SEM). The Si/Al ratio was determined by energy dispersive X-ray (EDX) performed with a EDAX-Phoenix (SUTW Detector, analyzer: Si/Li crystal).

The powder X-ray diffraction (XRD) patterns of zeolite samples were collected on a Philips PW 1730/10 X-ray diffractometer, at 2θ from 5 to 40° in steps of 0.02° (Ni filtered Cu Ka1 + Ka2, λ = 1.542 Å). The mean particle size was determined by dynamic light scattering (DLS) performed with a Zetasizer Nano ZS (MALVERN INSTRUMENTS, WORCESTERSHIRE, UK).

3. Results and discussion.

3.1 Design of the synthesis gel composition and synthesis conditions.

In the present study, FAU, one of the most widely used zeolites, has been chosen as case-study to describe our new synthesis procedure for nanozeolite production. The crystallization of an organic-free gel system has been triggered and addressed by using supported micron-sized NaX crystals. A schematic representation of the whole synthesis procedure is reported in Figure 1. With respect to our previous report,[40] the preparation of the FAU membrane has been avoided, thus providing a less expensive and time effective procedure. It is also worthy to remark that any organic linker or solvent was used for anchoring the NaX seeds on the support surface.
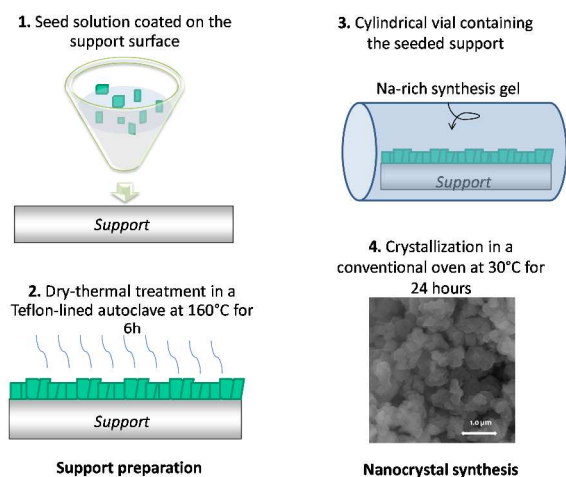

Figure 1. Schematic representation of the synthesis procedures for nanocrystals synthesis.

The synthesis was carried out at near ambient temperature condition (30°C) for a relatively short time (24 h) to prevent particle intergrowth and crystal growth. The starting precursor gel composition was opportunely adjusted mainly on the basis of the results previously reported in literature, for achieving an high degree of supersaturation and favouring a fast, abundant and homogeneous nucleation in the precursor system. Other criteria used for determining the synthesis mixture composition were: i) its ability to transform into the targeted zeolite (Y-FAU), ii) producing particles of nanometer dimension, and iii) obtaining an high degree of crystalline conversion in these "soft" conditions.

Within this context, Cardoso and co-worker recently reported a synthesis route for preparing FAU nanosized zeolite crystals in absence of organics.[32] They found that an increased alkalinity

of the synthesis gel was highly effective in determining a decrease in the final particle size. Accordingly, an hydroxyl-rich precursor gel of reduced water content having the following composition $4.3SiO_2:1Al_2O_3:15.2NaOH:321.4H_2O$, was prepared for this study.

The amount of seeds layered onto the support surface was ca. 2.5 (i), 5 (ii) and 10% (iii) with respect to the starting amount of SiO_2 used in the synthesis of the zeolite nanocrystals.

The crystallization was carried out at 30°C for 24 h in presence of the seeded supports. For comparative purposes, a reference sample was also prepared in the same synthesis conditions without the seeded support. After 24 hours, the seeded supports were removed from the reaction batches. The solid products, were recovered by centrifugation and dried at 80°C for 24 hours before characterization.

3.2 Phase and Morphology of the zeolite nanocrystals.

All the products were characterised by XRD, SEM, EDX and DLS analysis.
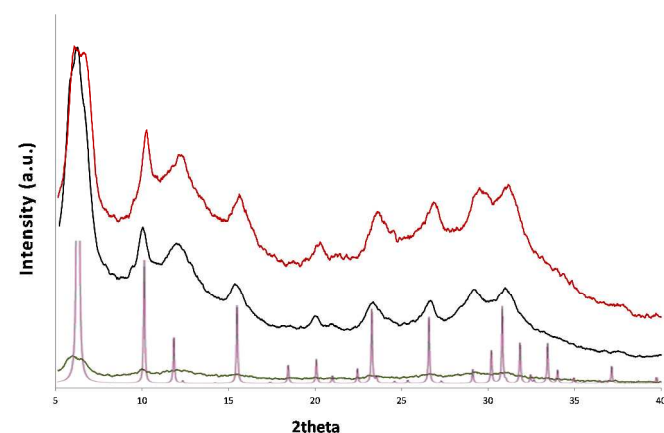

Figure 2. XRD patterns of the synthesized nanocrystals. From the top: Red line-unseeded synthesis (36 h). Black line-seeded synthesis (24 h). Grey line-unseeded synthesis (24 h). Magenta line on the bottom-reference pattern for a pure FAU phase.
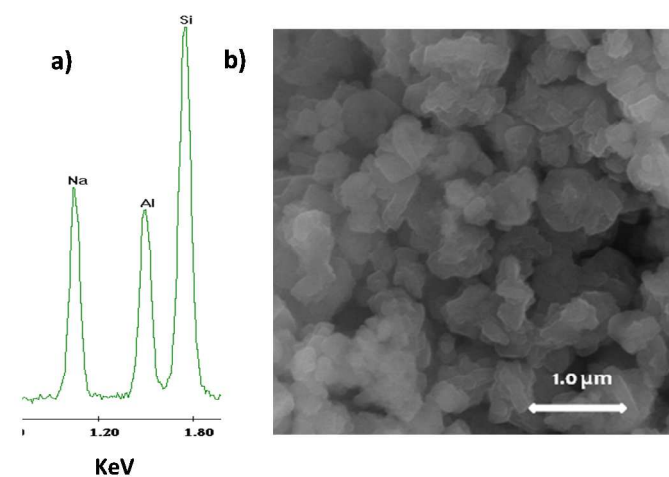

Figure 3. EDX (a) and SEM image (b) of the FAU nanocrystals synthesized by using the seeded support i).

The XRD pattern collected on the product obtained without using the seeded support shows that a nearly amorphous phase is formed after 24 hours of reaction (Fig. 2, green line). By prolonging the reaction time up to 36 hours, a poor crystalline product having the FAU zeolite structure is formed (Fig. 2, red line). As evidenced by the background hump (a halo spread on the whole window range) observed in the XRD pattern of the sample, an X-ray amorphous or short-order content is also present within the sample. The presence of amorphous phase has been also confirmed by SEM observations (Fig. S1a). The crystalline yield calculated with respect to the starting amount of SiO_2 was 21%.

The SEM micrographs show that the particle size was mostly between 150 and 200 nm, and abundant aggregates of irregular shaped particles are presents (Fig. S1b). DLS analysis was employed to accurately measure the mean particle size distribution. The sample was suspended in deionised water (1% wt/wt) and stirred for 1h before measurements. For separating physically adhered particles and achieving a better dispersion of the nanozeolites, ultrasonication was performed for 10 min on the same sample. DLS measurements performed before and after sonication provided a mean particle size of ca. 210 and 170 nm, respectively (Fig. S2).

Conversely, a higher degree of conversion of the starting gel system into a crystalline material took place within 24 hours when the seeded supports were used. The yield increases by increasing the amount of seeds, from 42 (i) to 51% (iii). The powder diffraction patterns collected on the samples obtained from the seeded solutions show diffraction peaks characteristic of the formation of a well crystallized, virtually pure FAU phase. The XRD pattern of the FAU nanocrystals synthesized by using the seeded support i) is reported in Figure 1. Peaks are broader and less intense if compared to the XRD pattern collected on commercial micron-sized FAU zeolites (Fig. S3), due to the reduced size of the synthesized particles. The chemical composition of the solids was determined by EDX. The Si/Al ratios was ca. 2 for all the samples, confirming the formation of a NaY-type zeolite (Fig. 3a).

Unfortunately, SEM images (Fig. 3b) show the occurrence of agglomerates in most of the samples. This phenomenon is not surprising, since nanoparticles tend to aggregate spontaneously and to form larger agglomerates in absence of suitable stabilising agents, thermodynamically driven by the resulting free energy decrease. Furthermore, we cannot completely avoid particle intergrowth, which usually occurs during the conventional seeded synthesis.[37] The agglomerates, whose size falls in the range of 100-200 nm, are formed by well-shaped plate-like nanocrystals of smaller dimension (ca. 30-70 nm). The presence of aggregates prevents an accurate evaluation of the mean particle size, due to the difficulty of clearly identifying the grain boundaries of individual zeolite crystals.

DLS analysis was performed on the samples prepared according to the previously described procedure and measurements were carried out on the same samples before and after sonication. In both cases, the DLS curves show a marked decrease of the particle size on going from i) to iii). Mean particle size distribution values of ca. 50, 55 and 59 nm were obtained before sonication for i), ii) and iii), respectively (Fig. 4). After sonication, the corresponding values were 35, 40 and 56 nm (Fig. S4). The slight differences in term of mean particle size observed on the samples after using sonication can be effectively due to the breaking up of agglomerates constituted by physically adhered particles, or more probably to the removal of amorphous impurities eventually covering the particle surface.
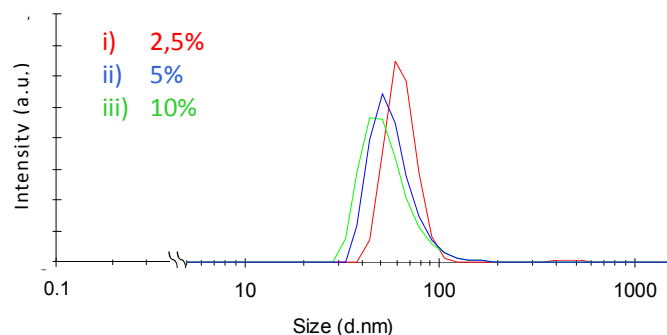

Figure 4. DLS curves of the synthesized FAU nanocrystals.

To certify that zeolite particles did not breakup during sonication, we prepared a reference sample by suspending micron-sized NaX crystals in deionised water (1% wt/wt). Ultrasonication was performed for 10 min and repeated cyclically for three times. The DLS curves collected on the same sample before and after each treatment (Fig. S5) showed no significant differences, proving that sonication does not damage the primary particles in the sample at list in our condition (low intensity and short application time), confirming the reliability of the results.

The values of the particle size depend on the amount of seeds anchored on the supports. In particular, the increase of the seeds from 2.5 to 10% led to a greater amount of smaller particles. By comparing the DLS data with the SEM observations, the employed amount of seeds seems to have a major effect on the degree of agglomeration, rather than on the effective size of the individual crystallites, in agreement with the results already reported in literature.[37] In particular, when a minor amount of seeds is used, a decreased level of aggregation is obtained.

We also try to quantitatively evaluate the size of the crystalline domains using the RDX data. In particular, we employed the Scherrer equation to estimate the size of the crystallites:

$$B = \frac{K\lambda}{L\cos\theta}$$

were B is the peak width, defined as the width of the diffraction peak, in radians, at half the maximum intensity (FWHM), K is the Scherrer constant or shape factor (considered as 0.94), L the mean size of the crystalline domain, λ the radiation wavelength and θ the diffraction angle.[41] A value of ca. 11 nm was obtained for the synthesized FAU nanozeolites i), when using the 533 peak ($2\theta \sim 23.5°$) which is significantly lower than the corresponding values determined by DLS.

With this respect, it is important to underline that L refers to the size of coherently diffracting crystalline domains rather than the actual particle size. Consequently, it may be smaller or equal with respect to the real particle size, since particles can be constituted by different crystalline domains (especially in the case of intergrown crystals). In addition, the important signal-to-noise ratio, the low intensities of the peaks and their low resolution make this method poorly accurate in our case.

It is also worthy to remark that the peak profile is a convolution of several contributions, which include, beside crystallite size, instrumental broadening, microstrains, non-uniform lattice distortions, faulting, dislocations, antiphase domain boundaries, grain surface relaxation, solid solution inhomogeneity, temperature, etc.[42] All these factors can contribute to peak broadening, leading to a sub-estimation of the particle size. More advanced analytic methods, such as the profile fitting of individual diffraction peaks or the whole XRD pattern modeling, would be required, but such a specific investigation on the crystalline domain size falls out of the immediate scope of the present investigation.

3.3 Discussion.

It is well established that the formation of small zeolite crystals requires conditions (supersaturation, low temperature,…) that favour nucleation over crystal growth. Moreover, before the crystallization starts, a critical mass of viable nuclei need to be produced and an homogeneous gel composition close to the zeolite stoichiometry has to be realized.

Conversely, the exact mechanism and the nature of active species that promote zeolite crystallization in a seeded system have been not fully identified yet.[43-45] As reported by Majano et al. in a recent nice paper,[37] a uniform distribution of seeds within an amorphous gel precursor favours the formation of nanoparticles with a narrow size distribution, since a greater number of viable nuclei are simultaneously formed in the gel system. Moreover, seeds smaller in size seems to increase the rate of crystallization more effectively with respect to larger ones.
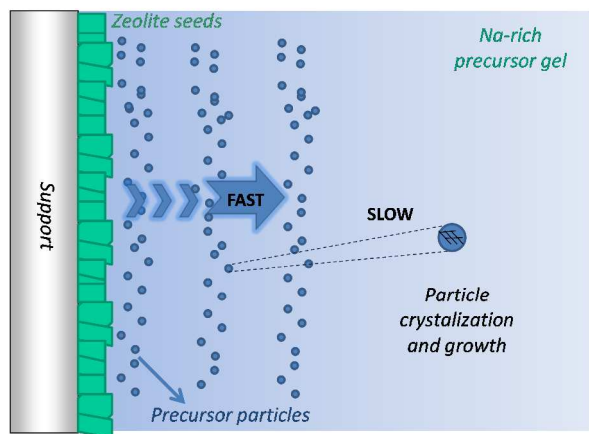

Figure 5. Schematic representation of the hypothesized mechanism for the formation of FAU nanocrystals.

In our case, the use of supported seeds joined to the suitable composition of the starting gel system most likely represented the key-factors for reaching a higher degree of conversion of the starting gel system into a NaY nanocrystalline phase at lower crystallization temperature. Indeed, our strategy effectively combines the main advantageous features of two different approaches, namely Na-rich hydrogel- and seeded-synthesis. Consequently, it can be expected that zeolite nucleation and growth proceed through a balanced combination of the corresponding distinctive mechanisms. In particular (Figure 5):

i) The seeded support definitely influence the gel evolution, assuring a faster nucleation rate and triggering the crystallization of nanozeolites. This is a well-established effect observed in conventional (hydrothermal) seeded synthesis, where seeds are uniformly distributed in the reaction batches. In our case, the micron-sized seeds anchored on the support, are not uniformly distributed in the synthesis gel. Actually, only the gel stratum in the close proximity of the support surface is in contact with the seeds. On the basis of our results, and taking into account the generally accepted concepts previously mentioned,[37] we can speculate that, in the early stage of the gel evolution, nucleation first occurs near to the seeded support surface, and then readily propagates through the gel system, the formed nanoentities being even more effective in promoting nucleation in the successive gel strata than the seeds themselves.

ii) These elemental units transform into a crystalline phase, apparently with a low growth rate at least in our specific condition. Indeed, the nucleation process is favoured over crystal growth at lower temperatures, since the activation energy needed for crystal growth is generally higher.[16-20]

iii) The high hydroxyl content of the precursor gel restricts the size of the formed particles. Indeed, despite the complexity of the mechanisms leading to zeolite nucleation and growth, it is clear that alkaline hydroxide determines the size of the precursor particles.[11,32] Specifically, during the initial polymerization of the aluminosilicate precursor, an increase of the concentration of sodium hydroxide in solution restricts the extent of the polymerization process and leads to the formation of smaller particles.

Our findings support these hypotheses, since the size of the formed particles fall in the nanometre range, even when aggregates are concerned.

4. Conclusions.

Several advantages definitely derive from the use of zeolite nanocrystals in many applications, where conventional micrometer-sized particles have poor effectiveness. However, many synthesis-related issues need to be solved to make these materials readily available.

The seeded synthesis of zeolite nanocrystals provide many attractive benefits with respect to the traditional methods. The absence of organic SDAs makes the synthesis eco-sustainable and cost-effective. The product obtained does not require calcination, thus avoiding unwanted and non-reversible post-synthesis aggregation. Finally, nanozeolites of different structural types and with higher Si/Al contents can be synthesized without using organic SDAs. Unfortunately, crystalline samples with broader particle size distribution with respect to the classical syntheses are usually obtained. Furthermore, difficulties in the separation of such nanosized zeolite crystals from the seeded reaction system restrict their production on an industrial scale.

Here, we provided a novel seeded-assisted route for preparing low-cost NaY zeolites having pure FAU structure, size dimension in the nanometer range and improved zeolite quality. A nanocrystalline product has been obtained in high yield in a relatively short time reaction (24 h) at near ambient condition (30°C), in absence of any SDAs. The use of supported seeds jointly to the opportune composition of the starting gel system have most likely been the key-factors for reaching a higher degree of conversion of the starting gel system into a NAY nanocrystalline phase at lower crystallization temperature.

The approach described in the present study effectively address some significant points related to the classical seeded syntheses and offers good opportunities for industrial applications. The use of a seeded support for seeding the starting gel is more attractive with respect to seeded solutions for the simplicity of the purification procedures and for the possibility of re-using the support in successive syntheses. With respect to our previously reported procedure,[40] it is less expensive and time-consuming since it does not require the membrane preparation. Finally, even if aggregates of much smaller crystalline entities are still present, they occur in a much minor extend with respect to previously reported seeded syntheses,[37] their mean size remaining in the nanometre range.

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Notes and references.

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Electronic Supplementary Information (ESI) available: SEM and DLS of the product obtained after 36h of reaction without using the seeded support. XRD pattern collected on micron-sized FAU zeolites. DLS of the product obtained by using the seeded supports after sonication. DLS of micron-sized FAU zeolites collected before and after sonication. See DOI: 10.1039/b000000x/

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