

Synthesis of Nay-Type Nanozeolites and Their Assembling into Microporous Membranes

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In this paper we report on a divalent procedure for the synthesis of FAU zeolites with particle size distribution in the nanometer range and for the concomitantly assembling of a uniform layer of a quasi-solid gel containing nanozeolite precursor species on the support surface.

The crystallization has been conducted at room temperature, in absence of organic structure directing agents (SDAs). A highly reactive sodium hydroxide rich hydrogel was used as starting synthesis system, while micro-sized zeolite crystals, preliminarily coated on the support surface before the synthesis, oriented and promoted the nucleation and crystallization processes. Nanosized FAU crystals with particle size of ca. 56 nm have been obtained after 24 hours. Alongside, a thick gel stratum was formed on the support surface, which contains FAU nanoparticles of 20-30 nm.

The gel matrix assembled on the support surface was used as starting material for the zeolite membrane synthesis and it was rapidly converted into a nanocrystalline layer upon hydrothermal treatment at higher temperature. The FAU layer has a thickness of ca. 2 μm and is constituted by closely packed nanocrystals, whose dimension is still 20-30 nm. The mass transport properties of the prepared membranes were probed by feeding dry single gases (N_2 and CO_2) at ambient temperature, obtaining low permeance and ideal selectivity higher than the corresponding Knudsen value.

The results reported in this study indicate that supersaturation as well as the elevated amount of sodium ions are synergistic factors to reach a high degree of conversion of the hydrogel into a nanocrystalline material at near ambient conditions and to induce the assembling of soluble aluminosilicate species on the support surface, thus effectively promoting the heterogeneous nucleation process.

1. Introduction

Zeolites with particle size in the nanometer range have been recently subject of intense research (Valtchev, 2013). The scaling down of the particles size promises to remarkably change the properties and performances of nanozeolites with respect to conventional zeolite materials (Holub, 2013). Indeed, nanozeolites profitably combine large external surface areas, tunable surface properties, high loading capacity, enhanced accessibility to the zeolitic microporous volume and reduced intracrystalline diffusion paths. As a result, limiting the size of the zeolite particles to the nanometer range has been an elegant strategy to limit the inefficient mass and heat transfer phenomena occurring in traditional zeolite-based catalysts and to introduce rich surface properties for the immobilization, separation and identification of biomolecules.

Typically, nanozeolites are produced as crystalline powders by hydrothermal treatment of synthesis gels or solutions (Tosheva, 2005). Most of these methods require the use of large amounts of organic templates for promoting the nucleation process and addressing the crystallization toward the desired zeolite phase. Nevertheless, this approach implies industrial and environmental concerns resulting from the use of expensive

and toxic organic templates and the need for high temperature post-synthesis treatments. Consequently, many efforts have been recently devoted to the develop organic-free synthesis procedures for nanozeolites preparation.

For many of the intended applications, however, the performance of the zeolite material results to be limited by its powder form. For instance in catalysis, zeolite powders are difficult to handle, causing the loss of significant amounts of material during the process set-up or zeolite regeneration and creating difficulties for the separation of the zeolite powders from the reaction products. These issues have catalyzed a vibrant research into the preparation of alternative zeolite materials to fully exploit the extraordinary zeolite properties. (Chen, 2012) The potential of zeolites prepared in the form of tailored structures has been realized for many traditional and emergent applications. In particular, the assembly of zeolite nanocrystals into supported layers or into other nonconventional macrostructures is a hot research topic in the field of modern zeolite science. Assembled nanozeolite layers have been evaluated for potential applications in catalysis (Mc Leary, 2006) and gas separation (Snyder, 2007), as well as for their use as promising low-k dielectrics (Wang, 2001), corrosion protective films and for biomedical related technologies (Zhou, 2007).

However, as already mentioned in the case of conventional nanozeolite syntheses, the traditional procedures for the preparation of zeolite layers and coatings often require many steps, toxic solvents and templates and special conditions, and cannot be straightforwardly scaled up at an industrial level. As a results, thanks to the recent technological developments and the increased awareness of environmental issues, there is a constant search for new synthesis roots to replace the existing technological solutions.

Starting from our recent results in the field of nanozeolites preparation (Mastropietro, 2014), we elaborated a divalent procedure for the synthesis of FAU nanozeolites and for the concomitantly assembling of a uniform layer of a quasi-solid gel containing nanozeolite precursor species on the support surface. The gel matrix assembled on the support surface constituted a suitable starting material for the zeolite membrane synthesis. Indeed, it was possible to rapidly convert the gel into a nanocrystalline layer upon hydrothermal treatment at higher temperature.

2. Experimental

2.1 Materials

Porous α - Al_2O_3 asymmetric tubes were used as supports (IKTS, I.D. = 7 mm, O.D. = 10 mm, length = 100 mm, dpore = 200 nm). The supports were rinsed in acetone in a ultrasonic cleaner for 1 hour, then boiled in distilled water for 1 hour and dried in a furnace at 100 °C for 2 h to remove any dusty and oily materials. NaX zeolite crystals (Sigma-Aldrich) having a mean crystals size of about 2 μm and a Si/Al ratio of 1.5 were used for seeding the inner supports surface. All the reagents used for preparing the reaction solution were purchased from commercial sources and used without further purification: Sodium Aluminate (Carlo Erba Reagenti, 53–55 % Al_2O_3), Sodium Silicate Solution (Aldrich, NaOH 14 wt.% and SiO_2 27 wt.%), Sodium Hydroxide (NaOH pellets, 97 %, Carlo Erba Reagenti).

2.2 Preparation of the seeded support

The supports were boiled in a NaOH solution 0.1 M for 1 h, in order to activate the unsaturated hydroxyl groups on the surface. The seeding procedure was carried out by carefully coating a seed suspension on the inner support surface to achieve a uniform deposition on the whole surface area. The amount of seeds (wt/wt %) layered onto the support surface was ca. 2.5 % 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 h without any solvent, to engender the condensation reaction between the seeds and the support.

2.3 Synthesis of FAU nanozeolites

A synthesis gel with the following starting molar composition: $4.3\text{SiO}_2:1\text{Al}_2\text{O}_3:15.2\text{Na}_2\text{O}:321.4\text{H}_2\text{O}$ was used for the synthesis of the nanosized zeolites. 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 h. After 24 h, 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 %.

2.4 Membrane preparation

FAU zeolite membranes were prepared by secondary growth method. After 24 h of treatment, the supports used for nanozeolites synthesis are uniformly covered by a thick gel stratum. They were isolated and transferred in a Teflon-lined autoclave for thermal cure of the synthesis solution, having the following molar composition: ii) $13.5\text{SiO}_2:1.0\text{Al}_2\text{O}_3:15.8\text{Na}_2\text{O}:509\text{H}_2\text{O}$. The autoclave was horizontally placed in the pre-heated furnace for the hydrothermal treatment at $80\text{ }^\circ\text{C}$ for 6 h. Before characterizations, the membranes were accurately washed with distilled water and dried for three hours at $50\text{ }^\circ\text{C}$.

2.5 Material Characterization

The morphology of the nanozeolites, the quasi-solid gel phase and the zeolite layer prepared in this work were investigated by using a Cambridge Zeiss LEO 400 scanning electron microscope. The Si/Al ratio was determined by energy dispersive X-ray (EDX) performed with a EDAX-Phoenix (SUTW Detector, analyzer: Si/Li crystal). The crystal phase of the nanozeolites, the quasi-solid gel and the zeolite membrane was identified by X-ray powder diffraction (XRD) performed with a Philips PW 1730/10 X-ray diffractometer (Ni filtered Cu $\text{K}\alpha_1 + \text{K}\alpha_2$, $\lambda = 1.542\text{ \AA}$). The mass transport properties of the membrane was measured by feeding pure gases (N_2 and CO_2) in dry condition at ambient temperature and operating *trans*-membrane pressure differences up to 1.2 bar. The zeolite membrane was housed in a tubular stainless-steel module sealed with silicon gaskets, having feed as inletting streams and permeate and retentate as leaving streams. The permeate flux was measured by means of a bubble-soap flow meter.

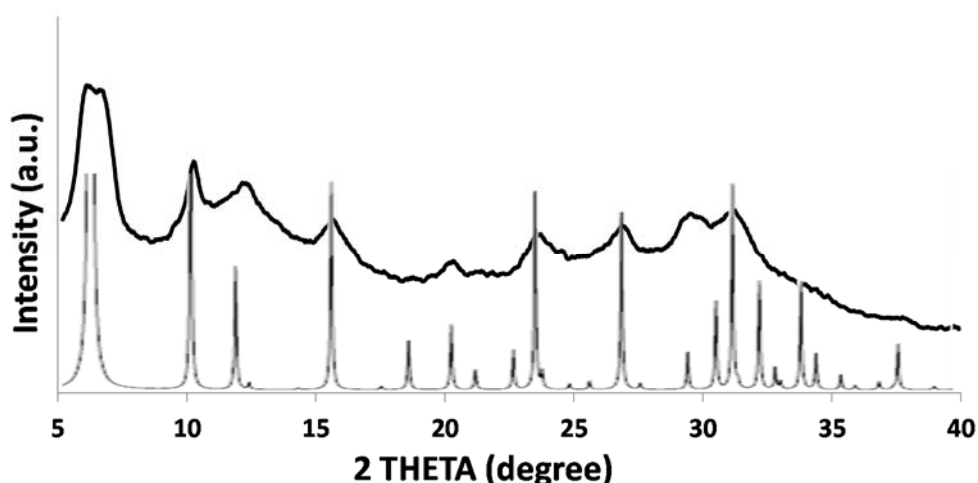


Figure 1: XRD pattern of the FAU nanozeolites synthesized after 24 h of room temperature treatment

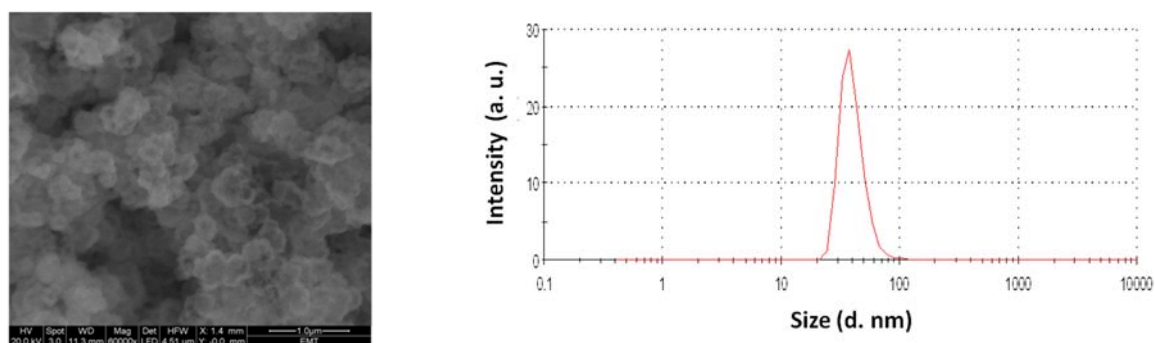


Figure 2. SEM image (left) and DLS graph (right) of the FAU nanozeolites obtained after 24 h of room treatment

3. Results and discussion

A high degree of conversion of the starting gel system into a crystalline material took place within 24 h at room temperature when the seeded support is used, with a final crystalline yield of 42 %. The powder diffraction pattern collected on the sample shows diffraction peaks characteristic of the formation of a well crystallized, virtually pure FAU phase (Figure 1). Peaks are broader and less intense if compared to the XRD pattern collected on commercial micron-sized FAU zeolites, 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. SEM images (Figure 2) show the occurrence of agglomerates, since nanoparticles tend to aggregate spontaneously and to form larger aggregates in absence of suitable stabilising agents. 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 dimensions of the primary particles constituting these aggregates was also confirmed by DLS analysis. A nanocrystalline sample was suspended in deionised water (1 % wt/wt) and sonication was performed for 10 min in order to separate eventually adhered particles and homogeneously disperse the nanozeolites prior to the DLS analysis. A mean particle size distribution value of ca. 56 nm (Figure 2) was obtained.

Beside allowing the production of zeolite nanocrystals in the hydrogel, the developed procedure concomitantly consents to realize an homogeneous coverage of the support surface with a suitable precursor material which can be successively converted into a nanocrystalline film.

In particular, a thick stratum of an heavily nucleating quasi-solid gel spontaneously deposits on the support surface in few hours. The gel structure is predominantly amorphous at the beginning. Within 24 h, several embryonic zeolite particles are formed in the gel matrix (Figure 3). The XRD pattern collected on the sample after 24 h of crystallization revealed the presence of single crystalline species with a sufficiently well ordered structure (Figure 4). As already observed in the case of nanocrystals, peaks are broader and less intense if compared to those corresponding to a micro-sized sample. However, on based on their 2 theta position, we can assume that a nearly pure FAU zeolite type phase is formed within the quasi-solid gel matrix. EDX analysis showed that the gel has a Si/Al ratio of ca. 1.7 and a Si/Na ratio of ca. 1.

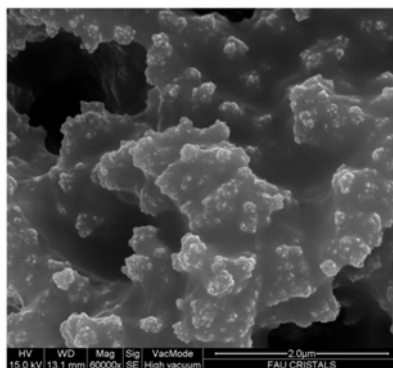


Figure 3: SEM image of the nucleated gel matrix showing zeolite precursor nanoparticles entrapped within the gel phase

The quasi-solid gel was converted into a fully crystalline nanozeolite layer by secondary growth, using a growing solution of lower alkalinity and reactivity having the following molar composition ii) $13.5\text{SiO}_2:1.0\text{Al}_2\text{O}_3:15.8\text{Na}_2\text{O}:509\text{H}_2\text{O}$. A thermal cure at higher temperatures boosted the crystallization of the zeolite precursor species, allowing the rapid conversion of the quasi-solid gel. Indeed, a polycrystalline zeolite layer was obtained within 6 h, the conversion being favored by the opportune chemical composition and the pre-existing organization of the gel network. RDX analysis performed on a sample scratched from the support surface indicate the formation of a well-crystallized, pure FAU phase (Figure 6). SEM images collected on the sample showed that the FAU layer has a thickness of ca. 2 μm and is constituted by closely packed nanocrystals, whose dimension was ca. 20-30 nm (Figure 7). No gaps, fractures or pinholes were visible on the whole surface analyzed. EDX analysis showed that the zeolite layer has a Si enriched composition with respect to the precursor quasi-solid gel phase, with a Si/Al ratio of ca. 2.5, and a lower sodium content (Si/Na ratio of 2).

The higher sodium content observed in the gel matrix proves the important role played by this cation in the early stage of the condensation process. We can speculate that electrostatic forces active between the

sodium cation and alluminosilicate anions most likely promotes the condensation of soluble precursor species into a quasi-solid gel matrix on the support surface. The diminished sodium content observed in the FAU layer suggest that during the hydrothermal crystallization of the gel matrix, sodium is expelled from the bulk of the transforming phase, since a minor amount of sodium is needed to balance the reduced negative charge of the zeolite framework.

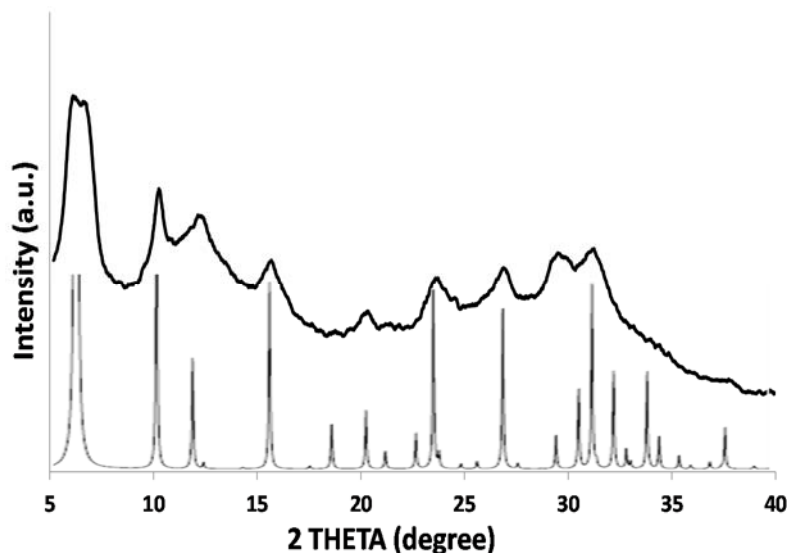


Figure 4: RDX pattern of the gel matrix formed on the support surface after 24 h of room temperature treatment

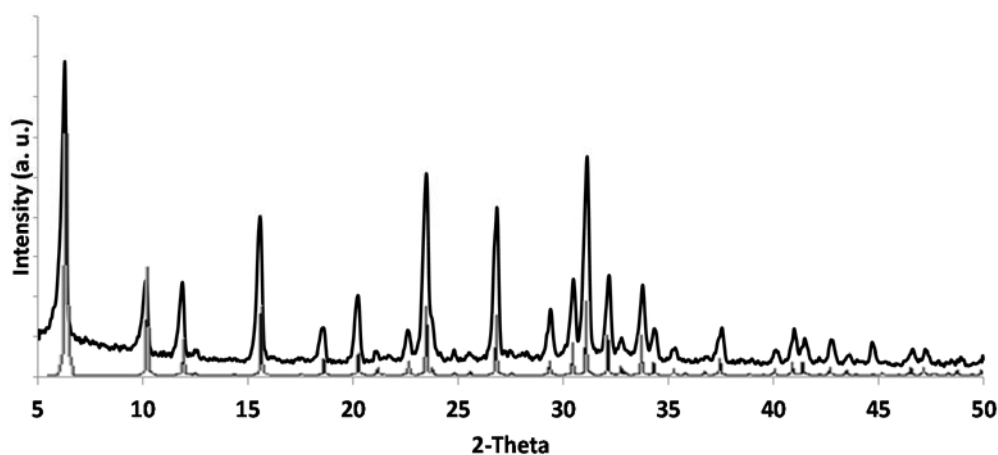


Figure 5: RDX pattern of the FAU nanocrystalline layer synthesized after 6 h of hydrothermal treatment

We did not observe a marked growth of the particles constituting the FAU layer with respect to the primary crystallites formed in the quasi-solid gel phase after 24 h. Consequently, the hydrothermal treatment essentially results into an increase of the degree of crystallinity and an enhancement of the cross-linking between individual nanoparticles. On the basis of these observation, we can speculate that the crystallization process of the gel matrix mainly takes place via propagation through the amorphous network with minor exchange of nutrients with the synthesis solution. On the contrary, the mean dimension of the nanocrystals formed in solution is higher (56 nm). Again, we can hypothesize that the nanoentities produced within the solid-gel phase can act as embryonic precursors of the zeolite nanocrystals formed in solution. Once formed,

some of these precursor species diffuse into the hydrogel phase, promoting successive nucleation and crystal growth.

The mass transport properties of the membranes have been estimated by feeding dry single gases (N₂ and CO₂) at ambient temperature. If compared to literature data, relatively low permeance were obtained (ca. $3.8 \cdot 10^{-9}$ molm⁻²s⁻¹Pa⁻¹ for N₂) and ideal selectivity higher than the corresponding Knudsen value (N₂/CO₂=3.1). No flux was observed in presence of humidity in this conditions.

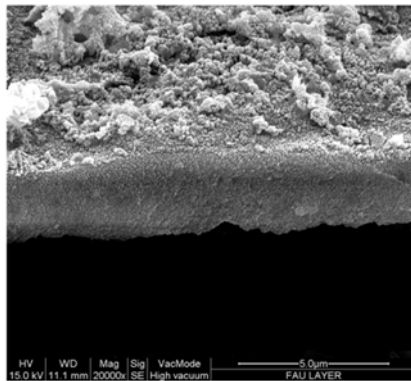


Figure 6: SEM side view of a self-standing fragment of the FAU nanocrystalline layer split from the support surface obtained after 6 h of hydrothermal treatment

4. Conclusions

The results of this study demonstrated that our synthesis procedure can effectively be used for preparing NAY zeolites having pure FAU structure and size dimension in the nanometer range. Furthermore, through the same procedure, it was possible to concomitantly assemble a quasi-solid extensively nucleated gel layer on the support surface. Owing to its suitable composition and structural organization, the gel matrix can be rapidly converted by hydrothermal treatment into a nanocrystalline FAU membrane.

It is worthy to remark that, since no organics have been used, this method allows to obtain nanozeolites as powders or directly and stably shaped into structured bodies, with no need of successive manipulations. The method is simple and of general validity and can be easily extended to zeolites of different topology.

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