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The Nanostructure Zeolites MFI-Type ZSM5

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Abstract

The development of new porous solids begins to provide effective and original solutions to the problems of pollution and sustainable development, and the challenge is to discover new performance of these materials. Among these materials are zeolites; however, one type has retained the attention since its discovery in 1972; this is zeolite-type ZSM-5, because of their particular properties in many industrial processes. These porous solids are characterized on the atomic scale by the existence of pores, distributed regularly in the matter and are likely to accommodate in their structures, gases, liquids, and solids for trap or temporarily store them. Only the average porosity of these zeolites constitutes an obstacle to the catalysis of cumbersome molecules that are well branched. To deflect this inaccessibility factor and trying to find a solution to this steric hindrance, the attention of the researchers was focused on using the surface properties of ZSM-5. It is well known that the efficiency and selectivity of a porous catalyst depends on its textural and structural characteristics and more precisely on the number of locations active on the external surface and the number of locations accessible through the porous system. The nanocrystallinity in the field of zeolites can be defined as a situation in which the physicochemical properties are largely determined by a larger number of atoms in the outer limit of crystallite. In this chapter, the work of several researchers who synthesized the ZSM5 in the field of nanostructures is presented. We find that, despite the different methods of synthesis, however, the field of nanostructures ZSM5 has been achieved. Certain parameters such as the concentration of mineral agent, the concentration of the structuring agent, and the duration of aging have a direct influence on the crystal size of the zeolites obtained. Different characterizations were used to identify the purity and size of the nanocrystals ZSM5.

Keywords: nanostructures, zeolites, catalysis, heterogeneous catalysts, ZSM5

1. Introduction

The discovery of a new family of inorganic materials composed mainly of silicon, aluminum, and oxygen has not ceased to attract growing interest and wide investigations. In 1756, Crönstedt [1], a Swedish mineralogist, discovered stilbite. He attributed it the name of zeolite which comes from the Greek *zeo* boiling and *lithos* stone (the boiling stone). Subsequently, the name zeolite was assigned to a family of natural aluminosilicic minerals. Their important scientific success and their kaleidoscopic applications are mainly due to the increasing progress made in synthesis (**Figure 1**).

Zeolites are hydrated aluminosilicates of the general chemical formula [2]: $M^{n+}_{(x/n)'} (AlO_2^-)_{x'} (SiO_2)_y (H_2O)_m$. Their properties depend in part on the value of the Si/Al ratio [3]. The structure of the zeolite crystals consists of an assembly of TO_4 tetrahedra (**Figure 2**).

The tetrahedron arrangement having two common oxygenated peaks leads to the formation of SBUs (secondary building units), which serve as reference patterns for classifying and describing the various structures of zeolites and their microporous networks [4, 5]; these structural types are made up of common genetic entities.

The secondary units are assembled in turn into polyhedra; this assemblage gives rise to the final structure. Each structural type obtained is assigned with a three-letter code according to the IUPAC nomenclature (International Union of Pure and Applied Chemistry).

It can be either an aluminum atom or a silicon atom. The arrangement of the tetrahedra in the three directions of space generates a large microporosity in which molecules will be able to adsorb and hence the name of molecular sieve given by Dr. José Walkimar Mesquita Carneiro (JWMC).

The zeolites are probably the only family that offers a great deal of structural and chemical diversity; several types are currently known and synthesized [6].

Figure 1. A natural zeolite “stilbite.”

Figure 2. Diagram of the assembly of SiO_4 and AlO_4^- tetrahedra.

Their major element is a tetravalent element of silicon “Si”; it is usually accompanied by a trivalent element, aluminum “Al,” iron “Fe,” barium “Ba,” and so on, and sometimes of a divalent element like beryllium “Be.” The presence of elements in the framework with valence lower than four led to the appearance of the negative charge, which is compensated by cations M^{n+} (generally alkaline earth) mobile and interchangeable with other cations.

The natural zeolites were considered as early as 1862, but the zeolite synthesis was not made for the first time until 1956 [7]. Today, the zeolite family includes more than 190 natural or synthetic aluminosilicates [4], each one is characterized by its own porous structure. This microporosity offers them many properties in the fields of adsorption, purification, and molecular sieving in separation processes. The synthesis of these materials is now well controlled, and the introduction of the quaternary ammonium cation type, as amines into the reaction medium, has allowed the development of many microporous materials related to zeolites such as aluminophosphates or gallophosphates. So far, 194 structural types exist [8], whose name is designated, according to the structure commission IZA (International Zeolite Association), by a code of three capital letters [9]. The particular porous structure of the zeolites, with pores and size channels at the molecular level, was at the origin of their properties (molecular sieves, large specific surface area, etc.). In addition, most of these materials possess an interesting thermal and mechanical stability compatible with industrial applications in various fields.

Their most important applications remain in the field of catalysis [10]. The zeolites are also used for their acidic and/or redox properties and their high regeneration capacity in petroleum refineries, for the cracking of heavy hydrocarbons in gasoline. The zeolites as faujasite (X or Y), beta, and ZSM-5 are the three most frequently used materials.

The MFI (Mobil-type five) zeolites [11] chosen as model adsorbents in this chapter are zeolites ZSM-5 (Zeolite Socony Mobil-type 5) [12]; they were synthesized for the first time in 1972 [13]. These materials are thermally stable up to 1000°C and their organophilic characters (due to Si-O bonds) and hydrophobic (due to their low content of charge-compensating cation) make them adsorbents and catalysts of choice.

The preparation methods of these zeolites are based on the same principle regardless of the type of the zeolite obtained. The bringing together of a source of element T, a solvent (H_2O), a mobilizing agent (OH^- , F^-), and a structuring and stabilizing species leads to the formation of a hydrogel simply called the “gel.” The hydrothermal crystallization of this gel leads to the zeolite being obtained.

The crystallization mechanism is based on the hypothesis of crystal formation in solution. The appearance of germs, then their growth, would be the result of condensation reactions between specified species present in the solution. The renewal of these species would be done by dissolving the solid phase of the gel [14].

2. Simplified description of the ZSM5 structure

Due to the complexity of the elementary lattice of zeolites, the structure of the framework is most often described by an ordered assembly of smaller unitary units [15] called SBU. Only the centers of silicon and aluminum tetrahedra are taken into account in this representation.

In the case of MFI zeolites [11, 16–18], the structure is defined from an arrangement of six SBU 5–1 tetrahedra (**Figure 3a**); SBU5–1 groups combine to form pentasil-like structural units (**Figure 3b**).

The arrangement of these chain groups (**Figure 3c**) leads to the formation of layers of tetrahedrons (**Figure 3d**) generally chosen to schematize the porosity of zeolites ZSM-5.

Figure 3. Elements constituting the structure of a ZSM-5 zeolite. (a) Type 5–1 SBU secondary construction unit. Assembly of secondary building units (b) in pentasil group, (c) in chain, and (d) in layers of tetrahedra.

The arrangement of the secondary building units generates a microporous structure composed of straight channels interconnected by sinusoidal channels within the MFI zeolites; **Figure 4** gives an illustration, and the channels have an elliptical opening, whose shape and dimensions vary according to the Si/Al ratio. In the case of zeolite ZSM-5, the right and sinusoidal channels have an opening, respectively, of the order of 0.54×0.56 and 0.51×0.55 nm². In the case of silicalite for an Si/Al ratio close to infinity, the sinusoidal channels become almost cylindrical (an aperture diameter of the order of 0.54–0.56 nm) while the right channels conserve an elliptical section with a dimension of the order of 0.51×0.55 nm² [19]. Three geometric sites are defined within the framework of MFI zeolites (**Figure 4**):

The sites (I): in the sinusoidal channels, of the order of $0.51 \times 0.55 \times 0.66$ nm³.

The sites (II): in the right channels with a dimension of $0.54 \times 0.56 \times 0.45$ nm³.

The sites (III): the intersection of the channels, with a volume of 0.9 nm³.

Figure 4. The channels of the ZSM-5.

3. Nanostructures ZSM-5

As already mentioned earlier, microporous materials have been widely used in chemical applications such as catalysis and in separations as adsorbents. However, there is another class which belongs to this category of porous materials, very promising in the catalytic act and in the separation processes; it is well characterized by its large external surface when compared with conventional zeolites, and they are the “nanocrystalline zeolites.”

It is well known that the efficiency and selectivity of a porous catalyst depends on their textural and structural characteristics and more precisely on the number of active sites on the external surface in relation to the number of locations accessible via the porous system. Any effect of crystal size of the zeolite is superimposed on the catalytic properties of the material involved, and the mass transfer properties of the catalyst.

For a long time, researchers have been interested in exploring new techniques in catalysis by inserting nanocrystals of zeolites into the framework of catalysts. Such beneficial effects of crystal size can be used in technical processes. So far, only a few examples have been reported in the study on the benefits of zeolite nanocrystals. These are effective even when they are inserted into the framework of the formed catalyst.

These cases relate to the insertion of zeolite beta nanocrystals into hydrocarbon hydrocracking catalysts, resulting in high yield and cracking activity due to the higher outer surface. In many other catalytic reactions, an effect of crystal size of zeolites has been demonstrated.

Aiming at the identification of a suitable route of ZSM-5 zeolite synthesis with acidic properties and crystal diameters of about 100 nm or less, we evaluate several methods of preparation adopted in the study and that been developed by ourselves. Two methods proved to be reproducible and successful. The first involves the hydrothermal crystallization of clear solutions under autogenous pressure, and this is the Van-Grieken method.

The other approach is based on the use of colloidal silicalite-1 grain crystals in open container crystallization (at atmospheric pressure).

The crystal size distribution and the Si/Al content of the products can be well controlled. The products of both types of syntheses could be transferred into their proton forms by conventional means without causing collapse of the crystal structure.

A large number of modifications in the original synthesis procedure have been developed since the discovery of ZSM-5 in 1972 [20]. In most catalytic applications, a decreasing crystal size has a positive effect because it promotes intra-crystalline diffusion. However, the use of very small particles involves the presence of a significant proportion of active sites on the outer surface of the zeolite and which can be detrimental if the effect of shape selectivity is exploited. As a result, a variety of methods have been developed to remove, neutralize, block, or deactivate these acidic sites [21–24].

However, recently, the acidity of the outer surface is considered a property of great interest when the zeolite is intended for the catalysis of reactions that involve bulky molecules

(not able to enter the microporous system) such as degradation of polymers or the cracking of heavy oils and in the production of fine chemistry, and so on [25, 26].

This is one of the main reasons explaining the great interest of nanocrystallines with a high external surface developed in recent years [27–34].

The nanocrystallinity in the zeolite domain can be defined as a situation in which the physico-chemical properties of these crystalline materials are largely determined by a greater weight of the atoms in the outer limit of the crystallite. Their difference in properties is no longer negligible [32].

The crystallization process of the nanocrystals of an MFI-type zeolite has been the subject of a number of works in recent years. Most of them focused on the crystallization of silicalite-1 with clear solutions producing crystals with sizes below 100 nm [35–42]. However, the crystallization of a nanocrystalline ZSM-5 in the presence of aluminum sources has not been studied in depth, despite the fact that the presence of aluminum is considered as an essential factor for obtaining materials with a considerable activity in acidic-catalyzed reactions.

Persson et al. [43] have studied the synthesis of crystals of a colloidal ZSM-5 with sizes in the range of 130–230 nm and a narrow particle size distribution. They found that an increase in the concentration of aluminum has caused a decrease in crystal growth, which implies a decrease in the size of the crystals [43].

Van Grieken [44] reported the synthesis of a ZSM-5 zeolite with sizes in the range of 50–100 nm at 170°C and at an autogenous pressure. He concluded that high alkalinity, a significant amount of water, and the presence of alkaline cations (such as Na⁺) are detrimental factors in obtaining nanoparticle zeolites. During the first hours of synthesis, the formation of an amorphous gel phase was detected, composed of particles with sizes below 10 nm. These primary units undergo an aggregation process to report secondary particles at sizes around 20 nm. The aggregation of the secondary particles leads to the formation of the final crystals of the zeolite with sizes in the range of 50–100 nm.

Reding [45] has compared different ZSM-5 nanostructure synthesis methods, concluding that the Van Grieken process [44] is completely reproducible and produces a product with good crystalline properties and moderately 90-nm crystal sizes.

4. Synthesis of nanostructure zeolites

Van Grieken [44] and Jacobsen [46] have given necessary descriptions of their methods of synthesis. Similarly, Verduijn's syntheses have been published in several patents. The possibility of synthesizing ZSM-5 with aluminum has been well recommended:

1. Synthesis from Verduijn [47] consists of a synthesis mixture of molar composition (9.12 TPA₂O, 60 SiO₂, 0.5 Al₂O₃, 936 H₂O) prepared by successively adding aluminum sulfate (Al₂(SO₄)₃·18H₂O, Merck) and silica to the solutions of tetrapropylammonium hydroxide (20% in water, Fluka). After stirring for 10 min under reflux, a homogeneous solution is

obtained. The hydrogel obtained was cooled to room temperature, and the mass loss due to evaporation is compensated by the addition of the deionized water.

The clear solution is poured into flasks equipped with reflux condensers and mounted in oil baths. The crystallization took place under atmospheric pressure and at static conditions for 12 days. The temperature is adjusted to 80°C.

The products are analyzed at different crystallization times. The products are recovered by centrifugation (at 5000 rpm), and the final product is washed several times with deionized water and then dried overnight at 120°C.

The result of this work is reflected in **Figure 5** which shows aggregates of nanoparticles.

2. Synthesis according to Van Grieken [44] consists of using aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, Merck), tetrapropylammonium hydroxide (TPAOH, 20% wt in water, Fluka), and tetraethylorthosilicate (TEOS, Sivento) to produce final synthesis solutions of composition: (10.7 $(\text{TPA})_2\text{O}$, 60 SiO_2 , 0.5 Al_2O_3). The crystallization is stopped after 48 h, and the product recovery is carried out as the above synthesis (**Figures 6 and 7**).
3. Synthesis of Jacobsen [46], the procedure is described using aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, Merck), tetrapropylammonium hydroxide (20%, Fluka), tetraethylorthosilicate (Sivento), and Printex L6 which is a carbon black with a pore volume of 1.2 mL/g (Degussa).

The synthesis mixture is inserted into the pores of the carbon black with the following composition: (10.8 $(\text{TPA})_2\text{O}$, 60 SiO_2 , 0.5 Al_2O_3 ; 468 H_2O : 240 EtOH). The use of carbon black consists in limiting crystal growth of the formed zeolite.

4. Atmospheric crystallization [48] with silicalite-1 grains involves one atmospheric crystallization procedure with grains of silicalite-1 used as seeds. This method of synthesis comprises two crystallization steps. In the first, a colloidal silicalite-1 is prepared according to the Verduijn procedure as described earlier, without the addition of an aluminum source.

After crystallization for 72 h at 80°C under atmospheric pressure, the nanoparticles of silicalite-1 were separated by centrifugation and decantation several times. In a second step, new synthesis mixtures were prepared by adding aluminum sulfate and silica to a solution of tetrapropylammonium hydroxide in water (20 wt%, Fluka), after 10 min of stirring under reflux and cooling.

The solution was seeded with colloidal silicalite-1 previously prepared. The resulting composition of the mixtures synthesis is as follows: (9.12 TPA_2O , 60 SiO_2 , 0.5 Al_2O_3 , 936 H_2O).

With: (60 (SiO_2) = a (SiO_2) silicalite-1 + b (SiO_2) solution).

The following images are taken with MBE scanning electron microscope, and this technique shows the existence of nanocrystals:

A: with a sowing of 10% of the weight in silicalite-1, and 8 days of crystallization;

B: with a sowing of 33% of the weight in silicalite-1, and 8 days of crystallization (**Figure 8**).

5. Belarbi et al. [49] tried the syntheses of the nanostructures ZSM5 in alkaline-fluorinated medium, instead of the hydroxyl medium used by the previous researchers.

The alkaline-fluorinated medium produces smaller crystal particles with crystallization faster compared to the first medium. As part of this work, they realized the synthesis of the ZSM-5 nanocrystals with the alkaline cation K^+ , and the use of this cation seems to activate the kinetics crystallization of ZSM-5 [50]. The use of fluorinated medium allowed the incorporation of insoluble elements such as Co^{2+} , Fe^{3+} , and Ti^{4+} carried out with moderation in a hydroxyl medium.

Figure 5. SEM image of a nanocrystalline ZSM-5 synthesized according to the Verduijn method [44] with the crystallization time of 12 days.

Figure 6. (a) DRX spectrum of a nanocrystalline ZSM-5 according to the Van Grieken method [44] with 12 days as the crystallization time.

Figure 7. MEB image of a nanocrystalline ZSM-5 synthesized according to the Van Grieken method [44] with 12 days as the crystallization time.

Figure 8. MEB image of a nanocrystalline ZSM-5 synthesized by two methods.

5. Synthesis method of nanostructures ZSM5 in alkaline-fluorinated medium

The following chemical products sodium silicate (63% SiO_2 , 18% Na_2O , 18% H_2O), aluminum sulfate octadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), potassium fluoride (KF), tetrapropylammonium

bromide (TPBr), demineralized water, and sulfuric acid H_2SO_4 1 N have been used to obtain ZSM5 nanostructures.

From a given molar composition, the following synthesis protocol has been involved [49]:

1. Solution (1): obtained by dissolving sodium silicate in deionized water under strong agitation at 60°C .
2. Solution (2): aqueous solution consisting of aluminum sulfates and potassium fluoride under intense agitation.
3. Solution (3): obtained by dissolution of tetrapropylammonium bromide (TPABr) in deionized water with stirring at room temperature.

Figure 9. Experimental protocol.

Still stirring, solutions (1) and (2) are poured dropwise on solution (3). The reaction scheme in **Figure 9** summarizes these steps.

The pH of the reaction mixture measured with a pH meter is usually in the order of 12. It is adjusted between 11 and 10.5 by the addition of sulfuric acid $1\text{ N H}_2\text{SO}_4$. The hydrogel obtained is placed in a ground flask, immersed in a crystallizer containing silicone oil (**Figure 10**). The crystallization of the zeolite is carried out under reflux under dynamic conditions (with continuous stirring). The synthesis is carried out at reflux of the reaction mixture (at 100°C), at atmospheric pressure, and for crystallization times ranging from 1 to 6 days.

At the end of crystallization, a biphasic (heterogeneous) solution was obtained, containing an aqueous and a solid phase. The material collected after centrifugation was washed several times with deionized water up to neutral pH. The obtained zeolite was dried overnight at a temperature of 100°C and calcined at 550°C for 8 h, so as to release its porosity.

Belarbi et al. realized the synthesis of nanocrystals ZSM-5 by varying several factors in order to optimize the mole composition of their hydrogel as well as the operating conditions of the syntheses. The products obtained are analyzed by different characterization techniques.

5.1. Influence of mineralizing agent concentration

The content agent mobilizer is studied in the reaction mixture from the composition of the following gel: 200 SiO_2 , $1\text{ Al}_2\text{O}_3$, $27\text{ Na}_2\text{O}$, $x\text{ KF}$, 20 TPABr , $7000\text{ H}_2\text{O}$ (with x between 5 and 40).

Figure 10. Different synthesis reactors (right autoclave) (left reflux system).

The experimental protocol is described previously; the spectroscopic analysis data by XRD showed that a crystallinity of 100% is recorded for the concentration of 20 moles of KF; beyond this concentration, a significant reduction of the crystallinity rate is observed. The effect of F variation on the crystallinity and quality of the product obtained is proposed by Guth [14], and the increase in the concentration of F ions leads to a growing number of defects in the structure of the product obtained (**Figure 11**).

5.2. Study of the aging time effect

The variation in the time aging was also optimized, and the step precedes the crystallization under reflux with continuous agitation. For a composition of the following reaction mixture: 100 SiO₂/Al₂O₃, 20 KF, 7000 H₂O, 27 Na₂O, and 20 TPABr at 100°C, the duration of crystallization was 8 days, and the aging time was varied from 0 to 92 h (**Table 1**).

The maturing time plays a very important role on the synthesis of zeolites by mainly decreasing the induction period and promoting the formation of the first germs.

Figure 11. The effect of KF concentration variation on the crystallinity level of ZSM-5.

Samples	Aging time (h)	Crystallinity rate (%)	Diameter (nm)
1NZSM5	0	75	—
2NZSM5	20	95	52*
3NZSM5	44	100	<25*
4NZSM5	68	98	<60*
5NZSM5	62	92	41*

*Estimation using MET.

Table 1. Effect of aging time on structural property.

Figure 12. The effect of aging time on crystal size and crystallinity rate of the ZSM5.

Figure 13. X-ray diffractogram of ZSM-5 at different aging times.

It was found in this study that when the hydrolysis time varied from 0 to 20 h, the crystallinity rate of ZSM-5 increased slightly; for an aging time of 44 h, the crystal size falls down from 52 to less than 25 nm; and for a longer aging period (samples 4 and 5), no appreciable change was observed. The supersaturation of the gel reaches its maximum after only 2 days of aging (Figures 12 and 13).

To better determine the size and morphology of the crystals, the transmission electron microscopy (TEM) technique was used; according to the TEM images represented in Figure 14, the prepared ZSM-5 samples consist of very small crystals, with size that varies from 15 and 25 nm. These crystals are not present as isolated particles, but in the form of small aggregates with sizes that exceed 200 nm.

5.3. The optimization of the organic template quantity

The quantity of organic template was optimized by varying its concentration from 0 to 40 moles, while keeping the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$, $\text{KF} = 20$ moles, $\text{H}_2\text{O} = 7000$ moles, $\text{Na}_2\text{O} = 27$ moles at 100°C for a period of crystallization of 6 days (Table 2).

The choice of TPABr (tetrapropylammonium bromide) as a structuring agent in the synthesis of zeolite ZSM-5 was been widely cited in the study [51]. This is due to the fact that this template plays a real role of template; in addition, it directs toward the structure ZSM-5. It

Figure 14. TEM (transmission electron microscopic image) of (A) N3ZSM5 with an aging time of 44 h (2 days) and (B) N4ZSM5 with an aging time of 68 h (3 days).

participates in the assembly SBU_{5-1} units and subsequently contributes to their stability. On the other hand, the geometry of the TPABr molecule promotes the rapid crystallization of ZSM-5 compared to the other organic structuring agents. This is explained by the low activation

Samples	TPABr/SiO ₂	Rate of crystallinity (%)	Diameter (nm)
N6ZSM5	0.4	100	20
N7ZSM5	0.3	82	33
N8ZSM5	0.25	78	48
N9ZSM5	0.2	71	52
N10ZSM5	0.1	30	70
N11ZSM5	0.05	21	—
N12ZSM5	0	5	—

Table 2. Effect of the template agent content on the size of formed crystals.

Figure 15. X-ray diffractograms at different TPABr/SiO₂ ratios.

Figure 16. TEM images of N6ZSM5 sample with TPABr/SiO₂ ratio = 0.4.

energy of this template $E = 83$ kJ/mole [52], compared, for example, with that of TEABr (tetraethylammonium bromide), which is equal to 90 kJ/mole [53].

Figure 15(a–d) represent the XRD spectra of the samples synthesized with TPABr concentrations ranging from 0 to 40 moles. The analysis of these spectra shows that the envelope of peaks between 7 and 10° (2 θ) and between 22 and 25° increases in intensity as the concentration of TPABr increases in the reaction mixture.

Sample A (**Figure 16**) was placed under the probe of an electron microscope transmission with sufficient magnification to see and even determine the size of the crystals which touches the field of nanometers, some of these crystals browse the size of 10 nm.

6. Conclusions

The screening of the research works concerns the synthesis of zeolitic nanostructures of the ZSM5 type, shown that in spite of the chemical elements that constitute these products which are the same, namely SiO₂, Al₂O₃, TPA₂O, H₂O, and Na₂O; however, the changes carried by the different authors in the source of these elements, the experimental protocol, and the methods of preparation allow to considerably affect the final size of the crystals of these zeolites. The work carried out for the synthesis of ZSM5 nanostructures in an alkaline fluoride medium has shown that certain operating parameters have a great influence on the quality of the final

product and on the size of these crystals. The operating parameters having a direct influence on the synthesis which include the mobilizing agent content F, the amount of optimal structuring agent used, and the aging time. The final etude shows that the optimum concentration is 20 KF, 40 TPABr, 100 SiO₂, 7000 H₂O, and 27 Na₂O. For an aging time of 44 h and for a crystallization time of 6 days and a crystallization temperature of 100°C, the crystal size of the nanostructures ZSM5 obtained was reduced until 25 nm.

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