



Article

Evolution of Morphology, Fractal Dimensions, and Structure of (Titanium) Aluminosilicate Gel during Synthesis of Zeolites Y and Ti-Y

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Abstract: Zeolite Y and Ti-containing zeolite Y (1%, 2% and 5% TiO₂) were synthesized by a hydrothermal seed-assisted method. In order to evidence the evolution of morphology, structure, and fractal dimensions during the zeolitization process at certain time intervals, a small volume from the reaction medium was isolated and frozen by lyophilization. The obtained samples were characterized by scanning electron microscopy (SEM), wide-angle X-ray diffraction (XRD), and small-angle X-ray scattering (SAXS). The fractal dimension values of the isolated samples, calculated from SAXS data, evidenced a transition from small particles with a smooth surface (2.021) to compact structures represented by zeolite crystallites with rough surfaces (2.498) and specific organization for zeolite Y. The formation of new structures during hydrothermal treatment, the increase in crystallite size and roughness due to the continuous growth were suggested by variation of fractal dimensions values, SEM microscopy images and X-ray diffractograms. The incorporation of titanium in low concentration into the zeolite Y framework led to the obtaining of low fractal dimensions of 2.034–2.275 (smooth surfaces and compact structures). On the other hand, higher titanium concentration (2%) led to an increase in fractal dimensions indicating structures with rougher surfaces and well-defined self-similarity properties. A mechanism for zeolite synthesis was proposed by correlation of the results obtained through morphological, structural, and fractal analysis.

Keywords: zeolite Y; Ti-zeolite Y; fractal dimension; surface fractals; zeolitization; seed-assisted synthesis; SAXS analysis; morphology evolution



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1. Introduction

In the 1980s, researchers were searching a theory that would give simple answers to complicated questions, such as describing complex geometry, far from Euclidean geometry, by a simple mathematical theory. When B. B. Mandelbrot introduced the notion of “fractal” [1,2], the theory proved to be a very useful tool for describing complex objects by a simple number—the fractal dimension and a property of “self-similarity”. The fractal theory was used to describe complex geometry such as: curves, aggregates, rough surfaces, and porous structures [1,2]; time-scaling processes and phenomena such as: diffusion-limited aggregation [3], cluster aggregation [4], percolation [2], and even fractal reaction kinetics [5]. In the last few years, designing materials with fractal properties seems to be an important goal in science: fractal catalysts [6–8], fractal antenna [9,10], and electronic materials [11]. Due to the interesting properties of the materials related to self-similarity, the property of a part to look like the whole was developed.

The mathematical description of self-similarity and fractal dimension is summarized in the following equation:

$$N(r/R) \sim (r/R)^{-D} \quad (1)$$

where D is the fractal dimension and $N(r/R)$ is the number of r -sized boxes that can cover an object of size R .

Real materials are not mathematically ideal self-similar objects but they exhibit fractal properties over a domain called the self-similarity domain. The beauty of the fractal theory is that it can describe very complicated porous, rough, and agglomerated structures using a fractional number: the fractal dimension and a domain, which the self-similarity limits [1,2,12,13]. Crossover and scaling behavior for the real system of fractal catalysts [12,13], reaction kinetics [12], and diffusion on fractal structure [13] were intensively studied since the 1980s. From the same research domain, zeolites with their interesting and complex structures are candidates with high chances of success to be described using fractal theory [14]. In addition, it seems that the evolution of the fractal dimension in zeolite synthesis can suggest the mechanism of the zeolitization process.

Zeolites, a class of microporous crystalline aluminosilicate materials with ordered cavities and channels [15] with micropores (~ 0.3 – 1 nm) were extensively studied and synthesized for their application in the chemical and petrochemical industry, air and water depollution processes, CO_2 capture, CO_2 degradation, biomass conversion, and fuel cell and thermal energy storage [16]. The diversity of zeolite applications is due to their special properties such as high adsorption capacity, molecular sieving, high thermal stability, shape selectivity, ion exchange capacities, and acido-basic properties [17]. Among the most urgent questions in zeolite synthesis are those concerning nucleation and growth of the zeolitic phase during hydrothermal treatment and the effects of various factors such as pH, temperature, presence of structure directing agents, and hydrothermal treatment time on zeolitization. Given the complexity of the zeolitization process, many experimental and theoretical techniques have been used [18–20].

The purpose of this work was to investigate the evolution of morphology, fractal dimensions, and structure of (titanium) aluminosilicate gel during the synthesis of zeolite Y, unmodified or modified with Ti, and the effect of experimental conditions on the crystallization process. All the aluminosilicate type structures that appear during the synthesis process of zeolite Y and the titanium aluminosilicate type structures in the case of the synthesis of Ti-zeolite Y materials were studied. Fractal dimension is a topic of interest that can help to explain more about the synthesis of zeolites [14]. Limited information on fractal dimension calculated from small angle X-ray scattering (SAXS) results are available in the literature [21]; however, there is no information available about the formation stages through the hydrothermal treatment. Zeolite Y, one of the most commonly used zeolites, is a faujasite molecular sieve with a three-dimensional microporous structure and a diameter of $7.4 \text{ \AA}$ [22]. Modification of zeolite by incorporation of Ti species into the framework leads to obtaining new valuable properties in heterogeneous catalysis, intensively exploited after the success of the TS-1 material [23]. The formation of zeolite Y and Ti-Y and the effect of titanium concentration by freezing the phases at various time periods were evaluated comparatively. We report here results on the structure and morphology of each phase, determined by X-ray diffraction and scanning electron microscopy. We associate the results of analysis with the values of the fractal dimensions calculated from the SAXS data. Moreover, a mechanism for zeolites synthesis will be developed by correlation of morphological, structural, and fractal data.

2. Materials and Methods

2.1. Materials

The chemicals used for synthesis of zeolite materials were sodium silicate (26.5 wt% SiO_2 , 10.6 wt% Na_2O , Sigma-Aldrich (Burlington, MA, USA)), sodium aluminate (NaAlO_2 , Sigma-Aldrich), $\text{Ti}(\text{ac.ac})_2$ (Sigma-Aldrich), and NaOH (98 wt%, Sigma-Aldrich).

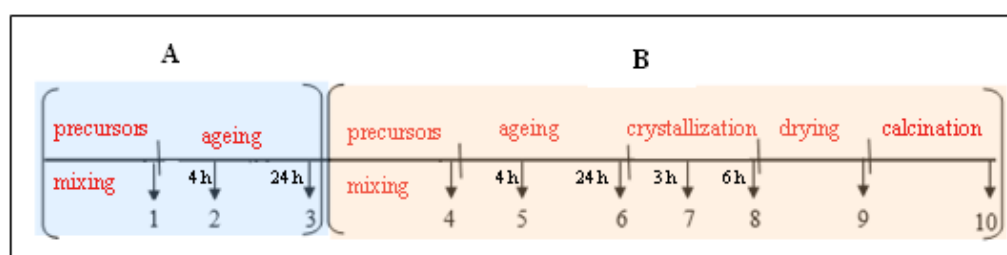
2.2. Synthesis of Y Zeolite and Ti-Y Zeolite

The zeolites Y and Ti-Y were obtained by hydrothermal seed-assisted synthesis according to the procedures previously reported by our group [24]. In the first step (A), we obtained the seed gel from NaOH/ NaAlO_2 (molar ratio 3.9) solution in which Na_2SiO_3 was added, under

stirring. The mixture was kept 24 h at 25 °C. In the second step (B), the seed gel was added in a sol–gel obtained from NaOH, NaAlO₂, and Na₂SiO₃, and was well dispersed in deionized water, held for 24 h at 25 °C, and aged 6 h in a Teflon-lined autoclave at 100 °C. After cooling down at room temperature, the product was filtered, washed with deionized water, dried for 12 h at 60 °C, and calcined for 8 h at 600 °C. The obtained sample was named Y. Ti-Y zeolites (noted xTY, x = 1, 2, or 5) were obtained by a similar method. Ti precursor (titanium(IV) acetylacetonate) was added under stirring, to a solution containing NaAlO₂, Na₂SiO₃, and 2 g of the obtained seed gel solubilized in NaOH solution (0.05 M). Then, three sol–gels were prepared with the following molar composition: 0.66Na₂O:0.21Al₂O₃:SiO₂:yTiO₂:19.1H₂O (y = 0.01, 0.02, 0.05), which were kept for 24 h at room temperature and then hydrothermally treated for 6 h at 100 °C in a Teflon-lined autoclave. The obtained solids were recovered by filtration, washed with deionized water until pH = 9, dried for 12 h at 60 °C, and calcined for 8 h at 600 °C. Thus, the obtained materials were named Y and xTY (where x = 1 or 2 and shows the percentage of TiO₂ in the sample).

2.3. The Zeolitization Stages

In order to evidence the growth behavior of aluminosilicate/titanoaluminosilicate sol during the zeolitization process at certain time intervals, a few mL from the reaction medium were isolated and lyophilized in order to freeze the process at a specific moment. The lyophilized products, used for further characterizations, were numbered from 1 to 10, depending on the stage from which the sample was taken, as described in Scheme 1.



Scheme 1. Numbering of the lyophilized samples obtained in A and B steps of the zeolite synthesis.

Thus, 1 was noted as the product obtained after lyophilization of the sample taken from the seed solution after mixing aluminate and sodium silicate in basic conditions (time $t = 0$); 2—sample from the sol–gel obtained after 4 h of aging; 3—sample from the gel obtained after 24 h of aging; 4—sample obtained after mixing of the seed gel with the sol–gel obtained in step B (time $t = 0$); 5—sample obtained after 4 h of aging; 6—sample of sol–gel after 4 h of aging; 7—isolated sample after 3 h of hydrothermal treatment; 8—isolated sample from the autoclave after 6 h; 9—sample recovered by filtration and dried at 60 °C; and 10—dry and calcined sample.

2.4. Characterization of Materials

The evolution of morphology and structure for the isolated and frozen samples during the zeolitization process were evidenced by scanning electron microscopy (ZEISS EVO LS10 SEM, Germany), EHT 10 kV, and X-ray diffraction at wide angles by means of a Rigaku Ultima IV diffractometer, Tokyo, Japan, with Cu K α ($\lambda = 0.15406$ nm) with a scanning speed of 1°/min. Phase identification was performed using Rigaku PDXL (version no 1.8, Rigaku, Tokyo, Japan) with Whole Powder Pattern Fitting (WPPF) module, connected to the ICDD-PDF-2 database. Small angle X-ray scattering (SAXS) measurements were carried out using a SAXSess mc2 (Anton Paar, Vienna, Austria) apparatus attached to a ID 3003 laboratory Xray generator (General Electric, Ahremburg, Germany), equipped with a sealed X-ray tube (PANalytical, $\lambda\text{Cu(K}\alpha\text{)} = 0.1542$ nm) operating at 40 kV and 50 mA.

2.5. The Fractal Dimension

There are a lot of methods used to determine the fractal dimension: adsorption isotherms [8], image-analysis using SEM, TEM, and AFM investigations [8], and small-angle scattering: neutron or X-ray (SAXS) [25–28].

In the paper, SAXS curve analysis was used to compute the fractal dimension. Scattering curves of $I(q)$ versus q , where $I(q)$ is scattering intensity and $q = 4\pi\sin\theta/\lambda$, with 2θ as the scattering angle, have different behaviors in different regimes. The limit region implies $qR_g \ll 1$ and the Guinier region is characterized by $qR_g \leq 1$. Meanwhile, the Porod regime by $a \leq q^{-1} \leq R_g$ and Bragg scattering regime by $q a = 1$ (R_g is the gyration radius of the scatterer and a is the basic building block size).

As previous studies showed, in the Porod regime, where $qR_g \geq 1$, there is always a domain where the following relation can be written [25–28]:

$$I(q) = I_0 q^{-\alpha}, \quad q = \frac{4\pi \sin \theta}{\lambda} \quad (2)$$

where I_0 is a constant and $\alpha > 0$. The slope of the log–log curve $I(q)$ vs. q , Equation (2), is related to the fractal dimension [21]. The mass fractal structures will exhibit slopes ranged between -1 and -3 , where the mass fractal dimension $D_m = \alpha$. Meanwhile, for the surface fractals, the slope will range between -3 and -4 and the surface fractal dimension $D_s = 6 - \alpha$ [25,26]. The domain of q where Equation (2) is obeyed defines the self-similarity domain, and it is a measure of the “fractality” behavior: a larger domain means that the structure is fractal over a large scaling domain and it is close to an ideal, mathematical fractal; a thin self-similarity domain will indicate a narrow scaling domain and weak fractal behavior. The mass fractal structures are polymeric, non-compact structures: structures characterized by higher mass fractal dimension D_m close to 3, will be denser. Meanwhile, lower fractal dimensions describe open, polymeric, non-compact structures. When the slope of the log–log scattering curve is ranged between -3 and -4 , indicating a surface fractal, the structure will have a compact, dense bulk, but a rough surface. Larger surface fractal dimension indicates a rough surface, meanwhile lower surface fractal dimension will indicate a smoother one. A surface fractal dimension close to 2 will indicate a smooth, non-fractal surface.

3. Results and Discussion

3.1. Morphological Investigation

Variation of morphology for the isolated and frozen samples during the zeolitization process (samples 1–10 from Scheme 1), respectively, the formation of building units during induction, nucleation, and crystallization steps, was investigated by scanning electron microscopy (Figure 1).

The synthesis of zeolite Y by the proposed method begins with the formation of seeds from Si and Al precursors in a basic medium (NaOH solution), which acts as the core in the subsequent zeolite synthesis. SEM images (Figure 1(1–3)) show the growth stages of these units that resulted by mixing sodium silicate and sodium aluminate in a certain concentration. The morphology of the crystallization germs is presented in Figure 1(3) and shows the presence of a continuous phase that includes viable nuclei for the formation of zeolite Y with a visible lower number of voids compared with the other two previous stages. The process of obtaining seeds involves many changes in the initial amorphous phase, leading to a gradual evolution of structural ordering, but without reaching the crystalline phase with a periodic lattice specific for zeolite Y.

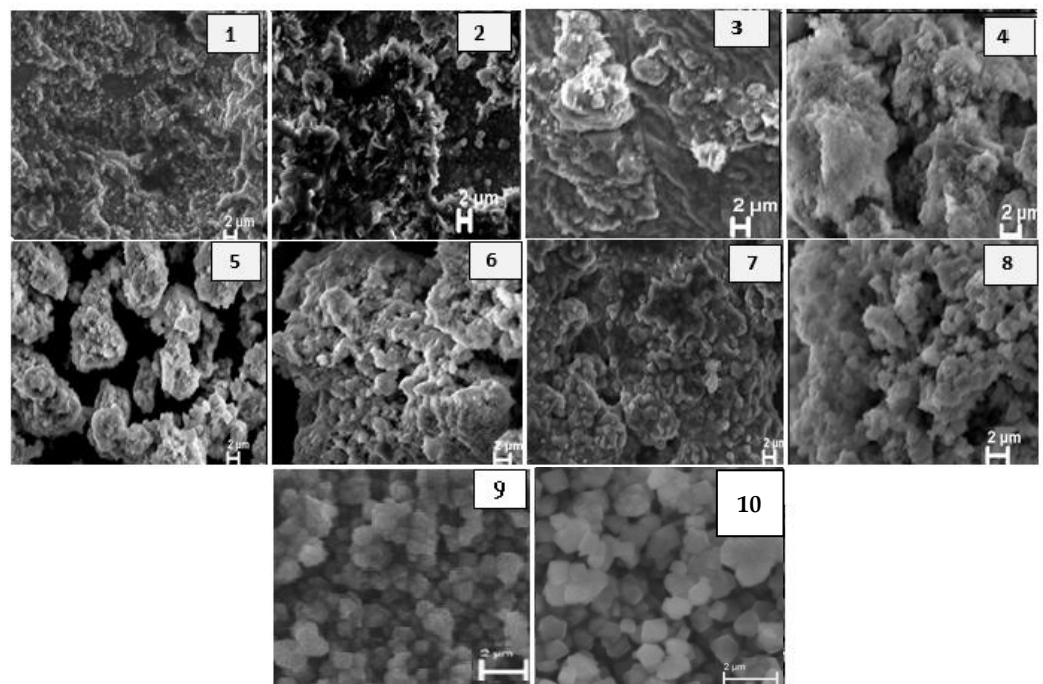


Figure 1. SEM images of lyophilized samples taken out during synthesis of zeolite Y (1–10, according to the Scheme 1).

The seeds used in the synthesis of zeolites increase the crystallization rate by providing the nuclei already formed, on the surface of which, amorphous aluminosilicate species gradually transform into crystalline structures during the aging process, and further, during the crystallization process [29]. Therefore, the use of crystallization seeds in the synthesis of zeolite Y clearly contributes to shortening the induction period allowing the direct transition of the existing viable nuclei to the growth stage through successive processes of polycondensation. The sequential morphological changes during the induction period are shown in Figure 1(4–6) from the starting moment of the reaction, when all the precursors were mixed, until the first crystalline species appears at the beginning of autoclaving, according to SAXS results (Figure 2). The use of zeolite Y seed crystals provided an active surface for the gradual uptake of aluminate and silicate species available in solution, as can be observed from the SEM images. All the structural changes during the growing period led to obtaining structures with a certain organization degree in order to facilitate the crystallization process (stages 7–8), triggered only in special conditions of temperature and pressure (autoclaving at 100 °C for 6 h). SEM images from Figure 1(9,10) show a typical zeolite Y morphology [30,31]. Therefore, the results obtained by SEM microscopy show the evolution of aluminosilicate sol–gel from the initial amorphous phase into ordered structures with gradually increasing sizes until the critical point where they reach sufficient dimension to be considered structural units in order to propagate periodically and to form the zeolite Y crystals. The different sizes of the species existing in the reaction system during the zeolitization process are also supported by the fractal dimensions, as will be discussed in the following section.

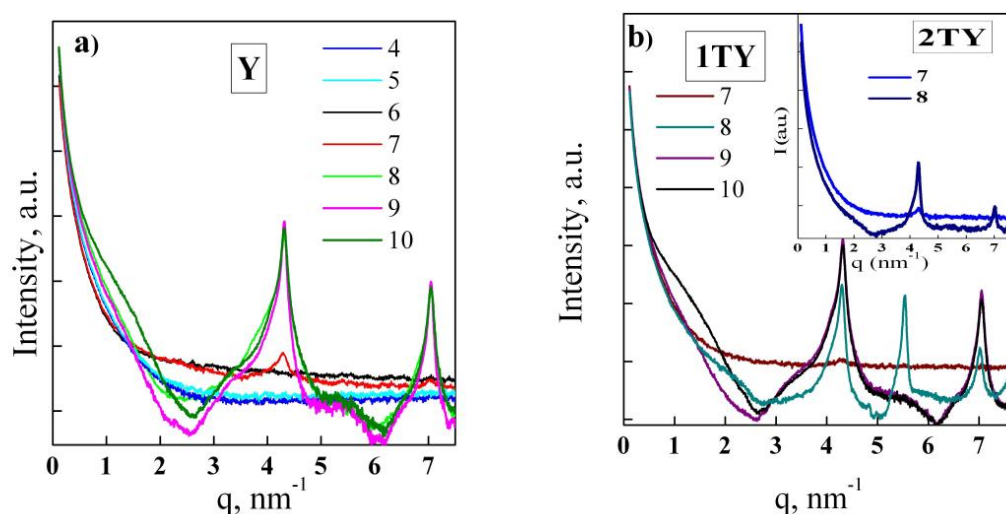


Figure 2. Scattering curves of the samples at different aging times. (a) Zeolite Y; (b) Ti-containing zeolite Y (1TY means zeolite containing 1% TiO₂ and 2TY means zeolite containing 2% TiO₂).

3.2. Structural Analysis

Scattering curves of the isolated and frozen samples at different aging times during synthesis of the zeolite Y (a) and Ti-containing zeolite Y (b) are presented in Figure 2.

The concave shape of the curves recorded for stages 4–7, at relatively low values ($q < 0.26 \text{ nm}^{-1}$), suggests the presence in the system of some small-sized structural units without forming crystalline species. From the stage corresponding to the end of the crystallization process, the shape of the SAXS curves becomes convex for values between $0.5\text{--}2 \text{ nm}^{-1}$, with the most obvious change appearing after the calcination step (sample 10). This suggests the formation of larger structures after calcination, as was also suggested by the calculated surface fractal dimensions (Table 1). These interpretations are supported by the wide-angle X-ray diffractograms (Figure 3) recorded for 1TY and 2TY materials during synthesis, which showed the appearance of diffraction lines characteristic for zeolite Y starting from stage 8.

Table 1. Surface fractal properties for Y, 1TY (1% TiO₂), and 2TY (2% TiO₂) systems in different stages of the zeolitization process.

Sample	$q \text{ (nm}^{-1}\text{) Self-Similarity Domain}$	α Slope	Surface Fractal Dimension D_s	Linear Correlation Coefficient (R^2)
Y (4)	0.1193–2.2019	3.979	2.021 ± 0.007	0.999
Y (5)	0.1194–2.2020	3.956	2.044 ± 0.008	0.998
Y (6)	0.1193–1.2891	3.986	2.014 ± 0.011	0.999
Y (7)	0.1199–0.4798	3.794	2.206 ± 0.009	0.999
Y (8)	0.1157–1.0026	3.914	2.086 ± 0.005	0.999
Y (9)	0.1141–0.1682	3.968	2.032 ± 0.004	0.999
Y (10)	0.1147–1.1045	3.502	2.498 ± 0.013	0.998
1TY (7)	0.1121–1.4169	3.966	2.034 ± 0.008	0.999
1TY (8)	0.1156–1.0668	3.996	2.005 ± 0.005	0.999
1TY (9)	0.1182–1.2109	3.934	2.066 ± 0.004	0.999
1TY (10)	0.1175–0.5674	3.725	2.275 ± 0.022	0.998
2TY (7)	0.1120–1.7447	3.929	2.071 ± 0.010	0.998
2TY (8)	0.1164–1.4919	3.867	2.133 ± 0.009	0.999

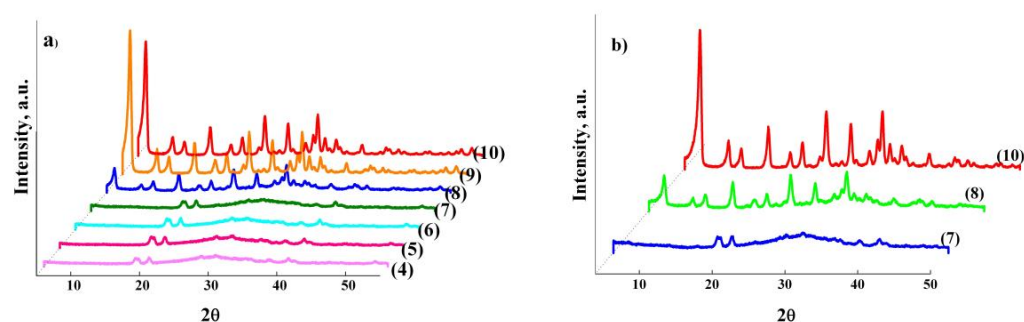


Figure 3. Wide-angle XRD patterns of Ti-containing samples at different aging times (Samples 4–10 from Scheme 1). (a) Zeolite Y with 1% TiO₂; (b) zeolite Y with 2% TiO₂.

Another important observation, highlighted by SAXS results (Figure 3), is given by the appearance of Bragg reflections at higher values, $q \sim 4 \text{ nm}^{-1}$, for samples taken during the crystallization stage (numbered 7,8), suggesting the presence of crystalline structures. Increasing the autoclaving time from 3 h to 6 h leads to signal intensification, probably due to the presence of more crystalline species in the system. This observation points out the fact that the crystallization process is triggered during the hydrothermal treatment, under specific conditions of pressure and temperature, as was also reported in the literature [32].

Wide-angle X-ray patterns recorded for 1TY in different steps of the zeolitization process (Figure 3a) evidenced the presence of some structures with a certain organization degree from the moment of seed addition into the reaction mixture (stage 4).

This observation is in accordance with the evolution previously described with the help of SEM images (Figure 1): the used zeolite Y seeds are developed structures, with a certain degree of organization, in the form of viable crystallization nuclei. From that point (stage 4) until the autoclaving step (stage 7), no change in the crystallinity degree was observed, X-ray patterns being identical. This is due to the fact that during the aging process, the propagation of the existing structures in the reaction medium takes place, leading to the formation of basic units for zeolite crystals. The formation of the highly organized zeolite framework occurs only under special conditions of temperature and pressure, as was suggested by wide-angle X-ray diffractograms (Figure 3) which evidenced the presence of specific diffraction signals for zeolite Y. It appears that the subsequent calcination process leads to a slight decrease in the crystallinity degree. The same observations are valid in the case of the 2TY material with a higher titanium loading. Increasing the concentration of titanium significantly influenced the crystalline structure of zeolite Y. The X-ray diffraction results indicate an amorphous structure for the resulting material [24].

3.3. Fractal Study

Fractal theory was used to explain the synthesis mechanism of zeolite Y and TY, considering that zeolite materials were obtained by the orderly connection of some structural fragments represented by primary, secondary, and tertiary units formed in solution during the synthesis process [33]. In the Porod regime, the fractal dimension is given by the slope of the fitting line from graphical representations of $\ln[I(q)]$ vs. $\ln(q)$, Equation (2), exposed in Figure 4 for zeolite Y and in Figure 5 for (titanium)aluminosilicates xTY ($x = 1, 2$).

By determining two fractal parameters such as the self-similarity domain and fractal dimension for the species in the system, the evolution of aluminosilicates during the zeolitization process can be prefigured. The slope of the fitting line from graphical representations of $\ln[I(q)]$ vs. $\ln(q)$, Equation (2), gives information regarding the type of fractal (mass fractals or surface fractals). Therefore, a slope between -3 and -1 indicates that the species are primary units, with open structures whose electron density is low. These are called mass fractals with dimension, D_m , equal to α . If the slope is between -4 and -3 , and this is our case as can be seen in Figures 4 and 5, it is considered that the analyzed species are surface fractals with dense, compact structures and their dimension D_s is $6 - \alpha$. A value of

$D_s = 2$ will indicate that the surface of the analyzed species is completely smooth, but the roughness degree of surface fractals will increase as the D_s value increases, too [34].

Fractal dimensions determined as previously described for the lyophilized samples collected during the synthesis of zeolite Y and 1TY and 2TY materials (according to the graphical representations from Figures 4 and 5) are presented in Table 1, along with the self-similarity domain, the slope, and the linear correlation coefficient. The surface fractal properties suggest that the analyzed samples in the case of zeolite Y synthesis have self-similarity properties over a large enough q -domain, characterized by fractal dimensions between 2.014–2.498. Slopes between -3 and -4 indicate surface fractal structures, meaning that the samples have compact structures and rough surfaces, starting from almost smooth surfaces (2.014) to medium-rough surfaces (2.498).

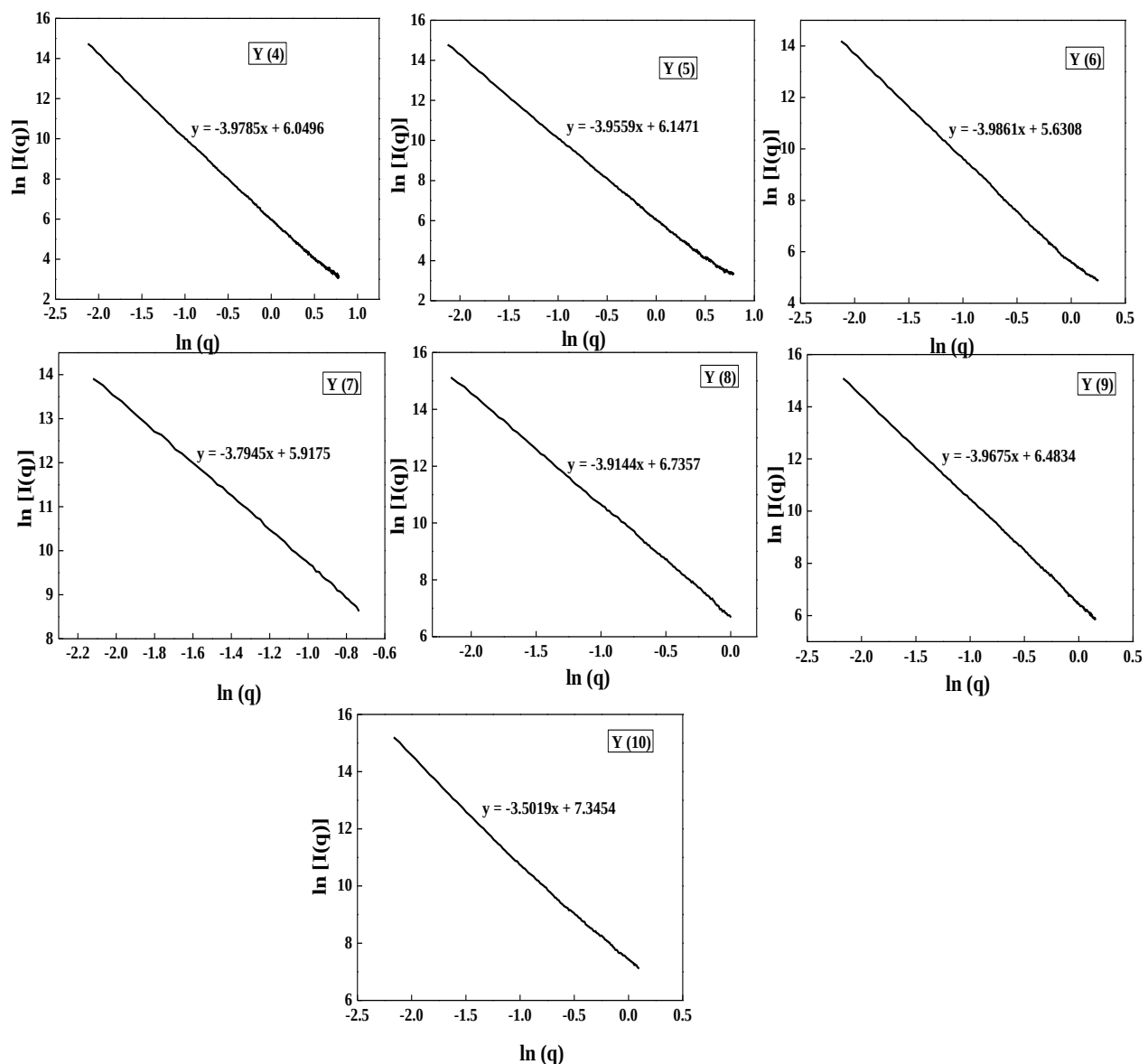


Figure 4. Graphical representation of scattering data from which the scattering exponent (α = slope) was estimated in the case of zeolite Y using linear regression. The best-fit equation is depicted for each data set.

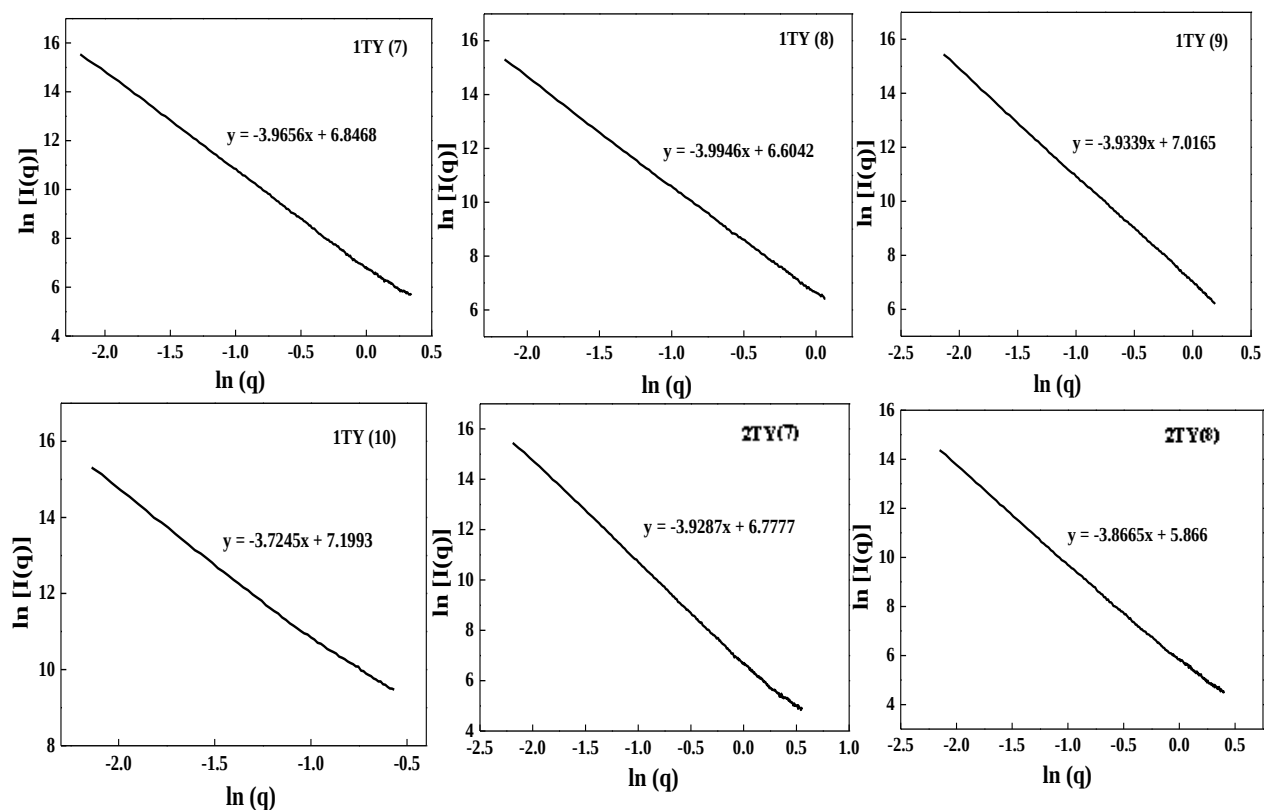


Figure 5. Graphical representation of scattering data from which the scattering exponent (α = slope) was estimated in the case of Ti-zeolite Y samples using linear regression. The best-fit equation is depicted for each data set.

The fractal dimensions determined in the case of zeolite Y synthesis, for the samples taken out during the precursor mixing step (stage 4), aging step (stages 5,6), and crystallization step (stage 8), are close to 2.00 compared with the sample collected at half of the crystallization step (stage 7) which presented the highest value recorded (2.206) but showed a narrow self-similarity domain. It can be stated that during the synthesis of zeolite Y, there is a transition from small and compact structures with smooth surfaces represented by zeolite Y seeds (stage 4) to zeolite Y crystallites with smooth surfaces and specific organization at the end of the crystallization phase (stage 8) via intermediate structures with dimensions and roughness increased, but low fractal behavior due to the continuous growth under hydrothermal treatment (stage 7).

The evolution of existing species in the system during the aging step (stages 5–6) is suggested by changes regarding the self-similarity properties, according to the results presented in Table 1. Thus, if at the beginning of the aging process, the self-similarity properties are recorded over a large enough q -domain (0.1194–2.2020), at the end of this stage, a narrowing of the self-similarity domain (0.1193–1.2891) will be observed, indicating the appearance of other species in the system, most likely with more advanced structures and with almost smooth surfaces (their size being very close to 2.00 value), which will serve as structural units for the formation of the zeolite Y framework during the crystallization process.

A notable narrowing of the self-similarity domain was recorded in stage 7 (0.1199–0.4798) which corresponds to the halfway crystallization stage. This behavior indicates the existence of an inhomogeneous system, with new species formed, whose structural properties are not defined in such a way as to present a similar character. The roughness degree of these species is higher, with the determined fractal dimension being 2.206. The formation of new structures during stage 7 was also highlighted by SAXS curves (Figure 2) which indicated the appearance of a signal characteristic for crystalline structures at $q \sim 4 \text{ nm}^{-1}$. At the end of the crystallization stage (stage 8), a decrease in fractal dimension was recorded, suggesting the formation of

structures with smooth surfaces and well-defined self-similarity properties. These species are zeolite Y nanoparticles with a crystalline structure, as shown using wide-angle X-ray diffraction (Figure 3). Moreover, widening the range of self-similarity in the case of stage 8 compared with stage 7, perfectly correlates with the intensification of the signal recorded at $q \sim 4 \text{ nm}^{-1}$ in the SAXS curves and suggests the presence of more crystalline species in the system.

Incorporation of titanium into the zeolite Y framework (1%) led to the obtaining of low fractal dimensions (smooth surfaces and compact structures) for 1TY(7), 1TY(8), and 1TY(9) samples, with self-similarity properties over a large q -domain. By increasing the titanium concentration in the system to 2% (2TY), the fractal dimensions are higher than in the case of 1% Ti (same stages), indicating the obtaining of structures with rougher surfaces than in the case of the 1TY material, with self-similarity properties over a large q -domain. Correlating all the results obtained through morphological, structural, and fractal analysis, we proposed a mechanism for zeolite synthesis (Figure 6).

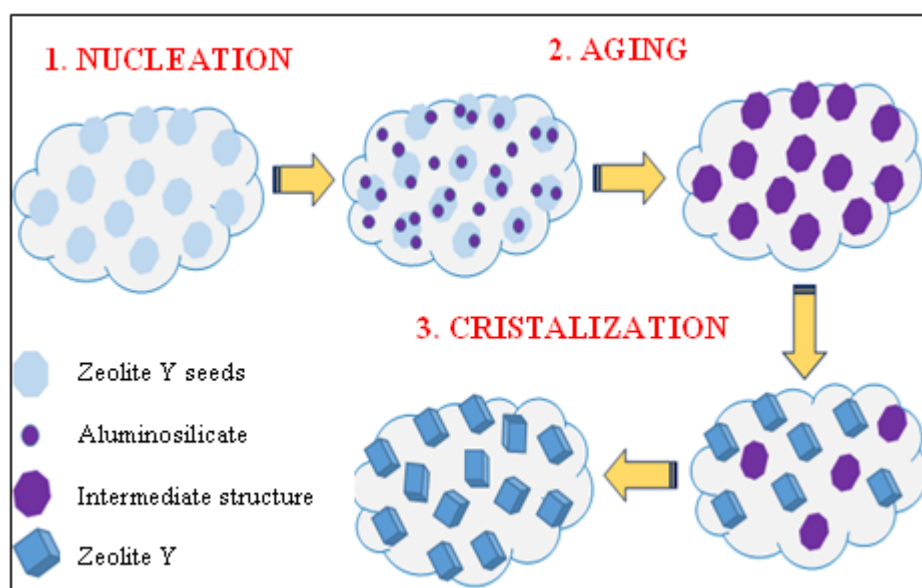


Figure 6. Graphical representation of the zeolitization process.

According to the same mechanism, (titanium)aluminosilicate-type materials (x TY, $x = 1, 2$) with a structure specific to zeolite Y are also obtained. Thus, in the first step, the formation of crystallite seeds from amorphous aluminate and silicate species takes place. These structures are characterized by small dimensions, smooth surfaces, and represent the nuclei around the basic units that form in the next stage (during the aging period) through the organized binding of Si, Al, and Ti species. At the end of this stage, intermediate structures in the system are obtained, which only under specific conditions of temperature and pressure turn into crystalline structures with typical organization for zeolite Y.

4. Conclusions

A new approach regarding the study of the formation of zeolite Y and Ti-Y crystals during the synthesis was proposed by combining SAXS analysis with fractal theory, SEM microscopy, and X-ray diffraction. Understanding the morphological evolution of zeolites in different zeolitization stages is an important step to design zeolites with the desired behavior. Our work is part of the scientific research related to this important domain.

The main novelty of the paper is using the fractal theory in order to characterize the transformations regarding the size and roughness of the structural units during the zeolitization of Y and Ti-Y materials and thus, based on fractal dimension, SEM characterization, SAXS, and X-ray diffraction, to describe the zeolite synthesis mechanism. Applying SAXS data to determine fractal dimensions for the isolated and frozen samples during the zeolitization of zeolite Y and titanium containing zeolite Y, evidenced transition from small

particles with low surface roughness (fractal dimension of 2.021) to compact structures represented by zeolite crystallites with rough surfaces and specific organization (surface fractal dimension of 2.498 and well-defined self-similarity domain). The formation of new structures during hydrothermal treatment and the increase in crystallite sizes and roughness due to continuous growth were suggested by the variation in surface fractal dimension values and SEM microscopy images. The morphological changes of the isolated and lyophilized samples confirm the importance of each stage in the formation of zeolite Y and Ti-Y. It was evidenced that temperature, pressure, and time of the hydrothermal treatment are key factors for the completion of the crystallization process. Moreover, according to our findings, adding TiO₂ in low concentration (1%) will decrease the surface fractal dimensions of the samples indicating smoother structures and low self-similarity properties. Meanwhile, by increasing the TiO₂ concentration, the structures will become rougher with larger self-similarity domains. The introduction of titanium into the zeolite Y network, by direct synthesis, and the effect of Ti concentration on the structure of zeolite Y have not been reported until now. A mechanism for zeolite synthesis was proposed by correlation of the results obtained through morphological, structural, and fractal analyses.

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