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Synthesis of ZSM-22 in Static and Dynamic System Using Seeds

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Abstract

ZSM-22 was synthesized using various sources of silica, organic template 1,6-diaminohexane, under hydrothermal conditions, with and without agitation during crystallization. Subsequently, the crystallized material was used as seeds to accelerate the crystallization process. Characterization of the ZSM-22 samples was performed by XRD, ATG/DTG and FT-IR. It was found that it is possible to synthesize ZSM-22 employing colloidal silica and pyrolytic silica as silicon sources only if the system is stirred during crystallization. The crystallization time for these systems was 13 hours, longer times of crystallization do not significantly increase the crystallinity of the sample. The addition of seeds significantly accelerates the crystallization of ZSM-22, reducing the crystallization time to only 7 hours, with stirring and with systems employing colloidal silica.

Keywords

ZSM-22; Seeds; Zeolite; 1,6-Diaminohexane

1. Introduction

ZSM-22 belongs to the group of medium-pore zeolite (mordenite family) which includes ZSM-5, ZSM-11, ZSM-35. It is rich in five-membered rings with wavy channels surrounded by ten-membered rings. The opening of channels (free diameter) is 0.45 × 0.55 nm running through the structure in a single crystallographic direction, having no intersections of the channels. The ten members channels of ZSM-22 are smaller than those found in ZSM-5, ZSM-11 and ZSM-35, however the determination of the structure of ZSM-22 indicated that its topology is similar to that of zeolite Theta-1 (TON structure type) is also similar to that found in the materials: Nu-10, ISI-1, KZ-2.

ZSM-22 in acid form is used in reactions such as: selective formation of p-dialquilbenzenes, enriched in

p-xylene C8 aromatics, alkylation of toluene with methanol selective for p-xylene and isomerization of 1-butene are particularly desirable in the petroleum industry. The acidic properties and selectivity of ZSM-22 have been addressed by many researchers in their studies [1]-[4].

Seed-assisted crystallization is a very useful method and has been used since the synthesis of the first zeolites in the mid-1960s, where the main function is to provide the system with the area over which the products are to be developed, avoiding the need for generation of this surface by the system itself, through primary nucleation. Its main effect is a reduction of the synthesis time, due to increased crystallization rate, resulting in materials with low impurity content [5] [6].

This paper studied the synthesis of ZSM-22, using 1,6-diaminohexane as the organic template, various sources of silica, with the SiO_2/Al_2O_3 ratio constant. Thereafter, the zeolite crystals were used as seed for further syntheses.

The challenge is to synthesize a copy of pure ZSM-22, since ZSM-5 and cristobalite impurities are difficult to avoid [7]. Different sources of silica are studied because their dissolution and reaction temperature determine the rate of crystallization of zeolite. Colloidal silica reacts rapidly to temperatures below 170˚C while the pyrolytic silica reacts readily at 170˚C [8].

2. Experimental

2.1. Synthesis of Zeolite ZSM-22 with Different Sources of Silica

For synthesis the following reagents were used: 1,6-diaminohexane as organic template (Sigma-Aldrich, 98%), potassium hydroxide (Sigma-Aldrich, 85%), colloidal silica (Ludox AS40, Sigma-Aldrich), pyrolytic (Fumed) silica (0.014 μ, sigma-aldrich), silica gel (Diasil 200, Diatom), cogel from the precipitation of silica of the commercial sodium silicate (Pernambuco chemical), aluminum sulfate hydrate (Merck) and distilled water.

The gel had the following molar composition: 27 $NH_2(CH_2)_6NH_2$: 13.5 K_2O: Al_2O_3: 90 SiO_2: 3600 H_2O, obtained following the methodology:

1) Solution A: Potassium hydroxide is dissolved in 30% of the total amount of water required for the synthesis;

2) Solution B: 1,6-diaminohexane is solubilized in 30% of the water required for the synthesis;

3) Solution C: aluminum sulphate is dissolved in 30% of the water required for the synthesis;

4) Solution D: silica dispersed in the remaining water of synthesis.

The procedure for preparation of the gel consists of: 1) adding solution B to solution A; 2) addition of the solution C; and 3) finally adding the solution D. At each addition step the system was agitated vigorously (with a mechanical stirrer) for 5 min at 400 rpm. The final gel obtained remained in this condition for 30 additional minutes.

For the agitated synthesis, the gel was transferred to a Teflon vessel with a volume of 700 mL. This container was placed inside a stainless steel vessel (with a volume of 1000 mL) in a Parr reactor model 4520. The reaction mixture was stirred at 400 rpm with a double helix impeller (with 6 blades on each rotor) while the system was heated from room temperature to 160˚C (within two hours).

For the static synthesis, the gel was placed in a Teflon vessel with a volume of 70 mL, and placed inside coated stainless steel autoclaves. Crystallization occurs at a temperature of 160˚C for periods up to 24 hours.

2.2. Synthesis of Zeolite ZSM-22 Using Seeds

The preparation method of the mixture and the synthesis conditions are the same as those described in the previous section. The seeds are added after mixing the solutions A-D, in the amount of 0.71wt% of the synthesis gel, and stirred for 15 minutes. Thus, the molar composition of synthesis was: 27 NH_2 $(CH_2)_6NH_2$: 13.5 K_2O: Al_2O_3: 90 SiO_2: 3600 H_2O plus 0.71 wt% seed.

2.3. Recovery of the Solid Phase after Crystallization

After crystallization, the autoclave was removed from the oven and cooled to room temperature. The content was transferred to a beaker containing 100 ml of distilled water and the resulting solid was separated from the supernatant liquid by vacuum filtration, washed several times with distilled water (until the pH of the filtrate reaches the value ~7.0) and dried in an oven at 120˚C for 12 h. In the case of the agitated synthesis (Parr reac-

tor), the reactor vessel was cooled by immersion in an ice-water mixture to speed up the washing procedure and the cooling and recovering the solid phase was similar to that employed in the static synthesis.

2.4. Characterization

The samples were subjected to X-ray diffraction (XRD) Shimadzu, model XRD-6000. The XRD profile was used to identify the material (type of crystal structure), the calculation of the crystallinity of the material was performed using Equation (1), using the peaks of 2θ regions of 19.7 to 20.9 and from 23.6 to 25 degrees.

$$\text{Crist.}(\%) = \left(\frac{\sum \text{peak area of the sample}}{\sum \text{peak area of standard sample}} \right) \quad (1)$$

The verification of presence of contaminating phases was done by comparison with published data in the literature and the diameter of the crystals [9], was done based on the Scherrer Equation (2), where the peak was chosen in the range of 19.7 to 20.9 degrees 2θ.

$$D_{hkl} = \frac{K\lambda}{\beta \cos(\theta)} \quad (2)$$

The thermogravimetric analyses (ATG/DTG) were performed in the thermobalance Shimadzu model DTG-60H, with a heating rate 10˚C/min in an atmosphere of synthetic air with a flow rate of 100 mL/min. From these analyses it was possible to quantify the organic template molecules and intracrystalline water present in the solid recovered from the crystallization process.

The absorption spectra in the infrared region (IR) were obtained with a spectrophotometer Fourier transform infrared Shimadzu, Model IRPrestige-21. The spectra were obtained in the range 400 - 4000 cm^{-1} by using KBr as a dispersing agent.

3. Results and Discussion

The initial phase of the study consisted of four syntheses varying the silicon source and keeping all other experimental parameters identical. The crystallization was carried out with stirring at 400 rpm, at 160˚C for 24 hours. **Figure 1** shows the X-ray diffraction (XRD) of the samples synthesized with colloidal silica and pyrolytic silica. From the comparison with the literature diffraction pattern [10] materials have been identified as zeolite ZSM-22 (TON structure).

The sample synthesized with colloidal silica had a higher crystallinity (~6%) when compared with the solid synthesized with pyrolytic silica.

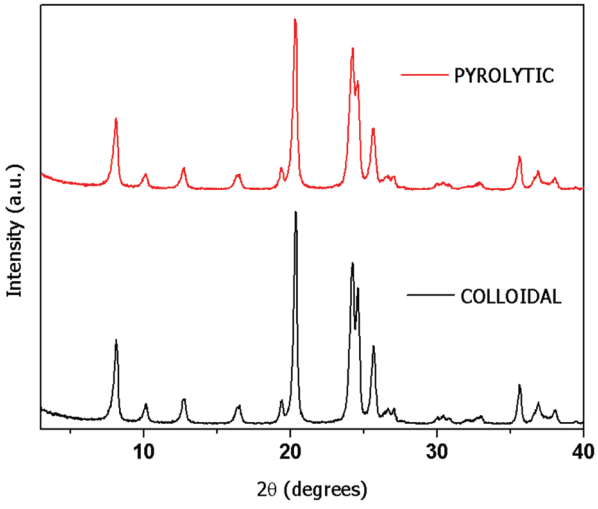

Figure 1. XRD of the samples crystallized under agitation employing colloidal silica and pyrolytic silica.

The samples with silica gel and cogel (compound solution resulting from the addition of aluminum sulfate + sulfuric acid diluted in a solution of commercial sodium silicate followed by filtration and washing) formed, respectively, the ZSM-5 zeolite and amorphous materials, as shown in **Figure 2**.

To verify the role of agitation on the crystallization of ZSM-22, a portion of the synthesis gel used in the experiments described above was transferred to a 70 mL autoclave and subjected to heating at 160˚C for 24 hours under static conditions. The results of the analysis of X-ray diffraction indicated that for all sources of silica studied there was no formation of crystalline material (only an amorphous solid). A similar result was obtained by Derewinski & Machowska [11] for synthesis with colloidal silica utilizing the same organic template used in this study.

The sample of ZSM-22 synthesized with colloidal silica with the highest crystallinity was identified, and then grinded and treated by ultrasound for subsequent use as seed material.

The gel composition chosen to assess the role of the seeds was the same as the one used to generate the seed, *i.e.* a system with colloidal silica and the same amount of organic template. The crystallization conditions were similar to those described previously for static and agitated experiments. **Figure 3** shows the XRD of the samples obtained with 24 h of synthesis.

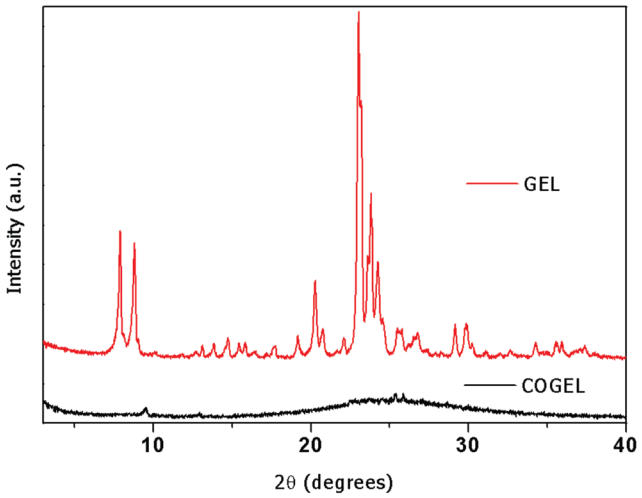

Figure 2. XRD of the samples crystallized with stirring using silica gel and the cogel obtained from sodium silicate.

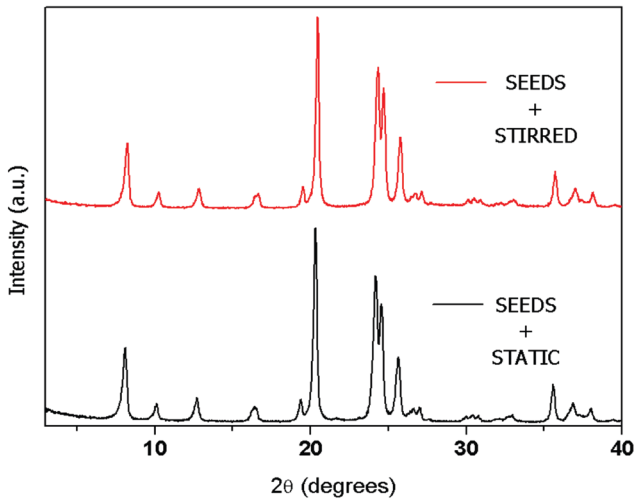

Figure 3. XRD of the ZSM-22 samples synthesized with seeds for static and agitated systems.

The experiment with seeds and agitation showed the highest degree of crystallinity (100% crystallinity of all the samples synthesized). Unlike the previous experiments without seeds, there was formation ZSM-22 in the system without agitation, but its percentage of crystallinity was slightly lower (~5%) compared to the agitated system.

In order to better understand the crystallization in static and agitated systems with addition of seeds, crystallization curves were constructed by periodic removal of samples, as shown in **Figure 4**.

In **Figure 4**, it is observed a rapid increase in the percentage of crystallinity of the samples from agitated systems—curves (a) and (c). It is noted that for the stirred seedless system the highest percentage of crystallinity was reached at 13 h. As for the stirred system with seeds, 100% of crystallinity was reached at 7 h. Therefore, the addition of seeds reduces by 4 hours the crystallization time to produce ZSM-22. In the case of static systems the addition of seed enables the formation of ZSM-22. However, the crystallization rate is slower than the one for stirred systems; the material is formed only after about 18h. This slower rate of crystallization is likely to be related to the difficulty in the diffusion of reactants within the reaction mixture to the surface of the growing crystal.

The average diameter of the ZSM-22 crystals was determined from the XRD patterns using the Scherrer equation, as indicated in **Table 1**. The data in the table indicates that crystals from seedless systems have smaller average diameters than the crystals obtained with seeds, as expected. This behavior may be due to two factors: 1) high speed stirring (400 rpm) prevents the formation of large crystals and 2) the use of seed introduces nuclei which speed the crystallization process resulting in larger crystals than for seedless systems. The calculated values for the average diameter of the crystals vary around 10%, because the calculation uses the peak areas from the XRD profiles where errors may surge from axial deviations, heterogeneity of the particles, preferential orientation, among others [12] [13].

The ATG/DTG curves of different samples of ZSM-22 synthesized in this work were very similar (**Figure 5**), having as the main feature four distinct events of mass loss.

These events were attributed to the following processes: 1) dehydration of the zeolite; 2) loss of organic template weakly bound to the surface of the material; 3) thermal decomposition of the organic template strongly bound to the surface; 4) loss of structural water by the condensation of silanol groups [4] [14] [15] and elimination of the fragments formed from the template decomposition.

The measurement of weight loss at each step was performed using a DTG curve and the data is summarized in **Table 2**. The mass loss events related to the removal of organic template (II and III) are responsible for about

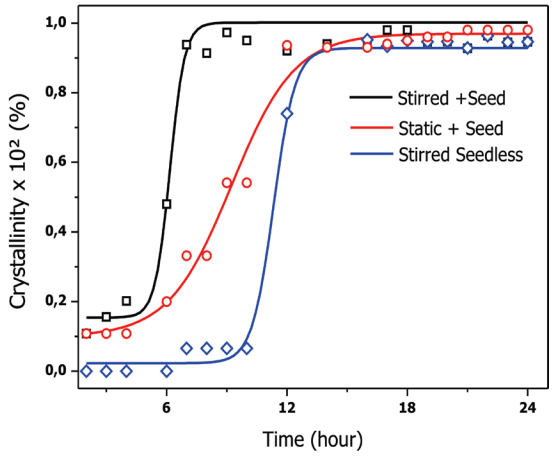

Figure 4. Crystallization curves. (a) Stirred + Seeds; (b) Static + Seeds; (c) Stirred Seedless.

Table 1. Average diameter of crystals obtained from the Scherrer equation for ZSM-22 samples with 24 hours of crystallization.

Sample	Colloidal Silica	Pyrolytic Silica	Stirred + Seeds	Static + Seeds
Average Diameter of Crystals (nm)	32	28	40	39

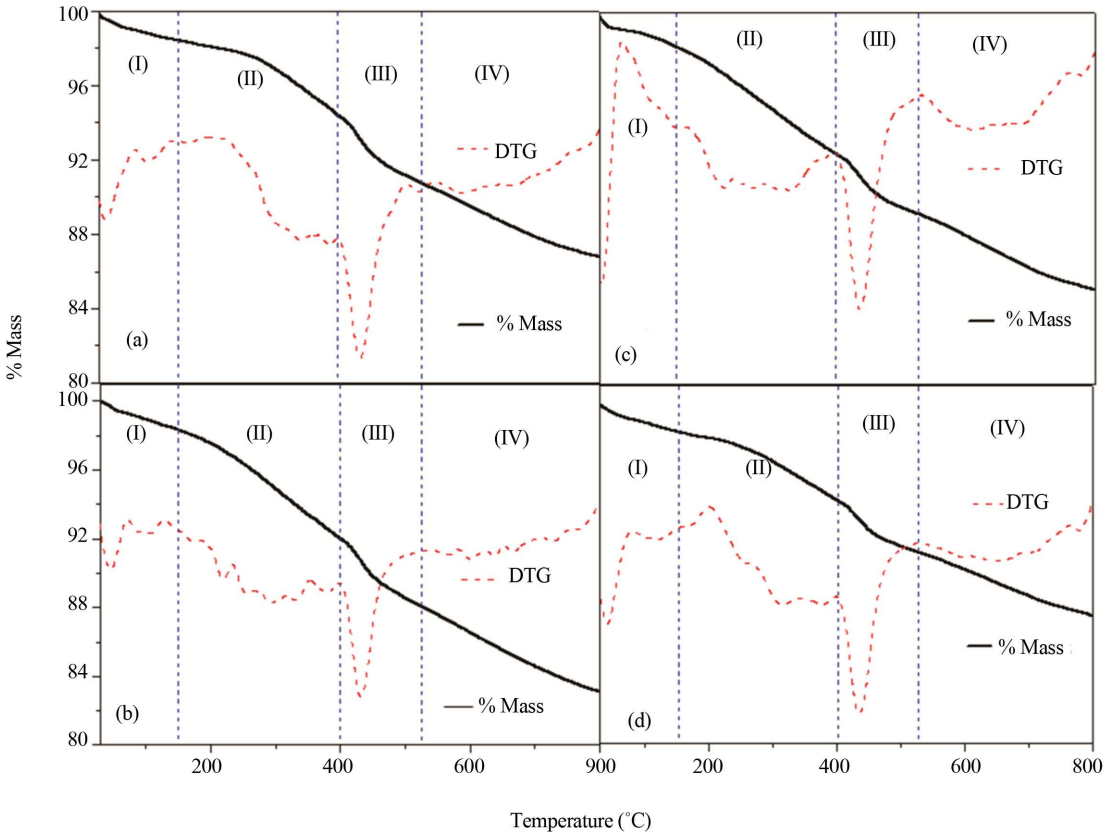

Figure 5. ATG/DTG curves. (a) Colloidal silica; (b) Pyrolytic silica; (c) Seed + agitation; d) Seeds + static.

Table 2. Temperature ranges and mass losses obtained by ATG.

Sample	Mass Loss (%)/Temperature (˚C)				
Events	**(I) 30 - 150**	**(II) 150 - 400**	**(III) 400 - 525**	**(IV) 525 - 800**	**Total Loss (%)**
Colloidal sílica	1.36	4.01	3.57	3.96	13.98
Pyrolytic silica	1.66	6.32	3.94	4.94	16.87
Seeds + stirred	1.63	5.81	3.17	4.06	14.67
Seeds + static	1.59	4.02	3.04	3.71	12.35

2/3 of the total sample mass loss.

Analysis of infrared spectroscopy for different ZSM-22 samples synthesized in this work are very similar. The spectrum for the most crystalline sample is shown in **Figure 6**. This curve shows five strong absorption bands in the region between 400 and 1500 cm^{-1}. The bands in at 1090 and 470 cm^{-1} correspond to the asymmetric stretching vibration type and flexion (T-O), for the internal tetrahedra. The band near 790 cm^{-1} is due to symmetrical stretching of the external tetrahedra [16]. In the range between 1500 and 4000 cm^{-1} (not shown) there are only two bands corresponding to large surface hydroxyl groups and intracrystalline water molecules. A striking feature of the spectrum is a shoulder band near 1220 cm^{-1} [17], which is typical of ordered silicates.

4. Conclusion

This work investigated the crystallization of ZSM-22 in agitated and static systems, and with or without the addition of seeds. It was found that it is possible to synthesize ZSM-22 zeolite free of impurities at 160˚C in the presence of 1,6-diaminohexane as the organic template using colloidal silica or pyrolytic silica as the silicon

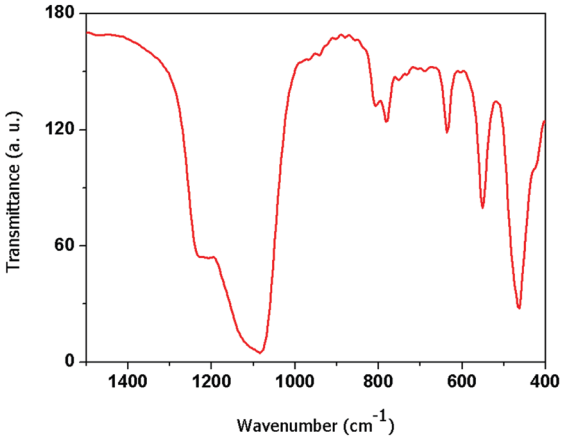

Figure 6. Infrared spectroscopy of ZSM-22 after 24 hours of crystallization without the addition of seeds with stirring.

source only if the system is stirred during crystallization. The shortest crystallization time with the highest crystallinity for agitated systems without seed material is 13 h. The syntheses with silica gel or cogel (humid solid formed by amorphous aluminosilicate) even with agitation, do not result in ZSM-22. The use of silica gel formed ZSM-5, while the use of cogel resulted in an amorphous compound. The addition of seed material significantly accelerates the crystallization of ZSM-22, reducing the crystallization time to only 7 h, for agitated systems using colloidal silica. Furthermore, the use of seeds allows the formation of ZSM-22 with colloidal silica without the necessity of agitation during crystallization. The average diameter data indicates that agitation at 400 rpm during crystallization or using seeds (in the case of static systems) favor the rapid crystallization of ZSM-22 resulting in very small crystals in the range 28 - 40 nm. Thermogravimetric analyses of the ZSM-22 samples show four events of mass loss and a total loss in the range between 12% to 14%.

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