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Study the Effect of Various Parameters on the Synthesis of ZSM-5 Zeolite

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ABSTRACT

ZSM-5 zeolite was synthesis under hydrothermal conditions at 175°C. The synthesis parameters have been investigated to find optimum synthesis method. Firstly, the crystallization time has been investigated to find the optimum crystallization time. Also, the ageing time was studied. The morphology, structure, and composition of the synthesized ZSM-5 zeolite were characterized using scanning electron microscopy (SEM), pH meter, viscometer, and X-ray powder diffraction (XRD). The bulk Si/Al ratio of ZSM-5 zeolite was in the range of 9.5—11.7. The synthesized ZSM-5 zeolite with appropriate ageing time could adjust crystal size and degree of the crystallinity. The crystal size of ZSM-5 zeolite obtained at an ageing time of 24 h was around 2.0 μm. The suitable aging time was 24 h, and the relative crystallinity of ZSM-5 zeolite could reach up to 100% after crystallization for 48 h at 175°C

Key Words: ageing time, Crystallization time, ZSM-5, crystal size.

دراسة العوامل المختلفة المؤثرة في صناعة الزيولايت ZSM5

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الخلاصة

تم تصنيع الزيولايت 5ZSM تحت الظروف هايدروحرارية في درجة حرارة ١٧٥ درجة مئوية. حيث تم دراسة العوامل المؤثرة على عملية التصنيع(تاثير زمن البلورة وزمن التنوية). كذلك تم تشخيص كل من الشكل السطحي والتركيبة الكيمياوية والهيكل البنائي الداخلي للزيولايت من خلال عدد من الفحوصات باستخدام المجهر الالكتروني ، ومقياس درجة الحموضة، و مقياس اللزوجة،و جهاز الاشعة السينية . وكانت نسبة السلكون الى الالمنيوم في النماذج تتراوح بين (٩,٥-الى ١١,٧. قد وجد انه بالامكان السيطرة على حجم البلورة ودرجة التبلور من خلال السيطرة علي زمن التنوية. وجد ان حجم بلورات الزيولايت التي تم الحصول عليها في٢٤ ساعة حوالي ٢ مايكروميتر وبدرجة تبلور تصل الى ١٠٠٪ خلال زمن تبلور مقداره٤٨ ساعة وبدرجة حرارة مقدارها ١٧٥م° .

1. INTRODUCTION

The ZSM-5 is a member of MFI zeolite pentasil family that consists of ten membered rings with a medium pore zeolite of 5.4–5.6 Å, **Catlow, 1992**. The ZSM-5 zeolite is well known as a catalyst in the petrochemical and refinery processes due to their novel structure, thermal stability, shape selective and acidity, **Rallan, et al., 2015.**

Generally, ZSM-5 is synthesized under hydrothermal conditions at temperature higher to 180°C. The reaction gel contains source of silicon and aluminum with a template, **Chou, 2006**. The hydrothermal process occurs by transformation materials phase from an amorphous to crystalline phase in the caustic solution. The mechanism of crystal growth occurs fast when applying ageing process prior to the crystallization process to produce seed gel for a synthesis process**.** Ageing time applied is to homogenize the amorphous aluminosilicate gel prior to the crystallization process at 25°C or slightly higher temperature, which is lower than the crystallization temperature, **ALRubaye, 2013.**

   The synthesis parameters have great effect on zeolite properties; these parameters such as ageing time, crystallization time, and crystallization temperature etc., are found to have influence on crystal size, Si/Al ratio, and degree of crystallinity. The ZSM-5 zeolite selectivity and efficiency depend on the number of active sites accessible via pore system. Crystal size can affect the mass transfer resistance through imposing a shorter diffusion path by reducing the ZSM-5 particle size, **Nagamatsu, et al., 1992**, **Yamamura, et al., 1994**. Therefor, the zeolite crystal size reduction has a huge impact on the activity and catalytic properties such as, catalyst selectivity, **Abrishamkar, et al., 2010**. Therefor, tailoring the size of the ZSM-5 crystal depends on the selectivity and activity of the catalyst and in which process it will be used is crucial, **Xue, et al., 2012.**

There are two methods for optimizing the size of ZSM-5 crystals; the first method is including the synthesis techniques or modification of synthetic parameters that is known as "Down-top ". And the second method is including the post-synthesis modification of synthesis zeolite that is known as "Top-down ",**Valtchev, et al., 2013**.

The aim of this investigation is to study the effect of the different factors such as crystallization and ageing time in down–top method in synthesis procedure and the influence of each parameter on the size reduction and crystallinity of ZSM-5

2. EXPERIMENTAL WORK

The ZSM-5 zeolite was synthesized under hydrothermal conditions following the procedure described in **ALRubaye, 2017**. The synthesis was carried out in two-step gel preparation. The first step is a batch composition with Al-free as seeding gel ($4.5Na_2O: 3TPAOH: 60SiO_2: 1200H_2O$). This is achieved by dissolving the weighted amount of sodium hydroxide (pellet, Sigma–Aldrich) in 1/3 liter of deionized water, then adding the tetrapropylammonium hydroxide (1M, Sigma–Aldrich) with $TPAOH/SiO_2 = 0.0033$ ratio, followed by the adding of colloidal silica (Ludox AS–40 from Sigma–Aldrich) gradually into caustic solution with continuous mixing. The gel was capped in a polypropylene bottle and mixed using magnetic stirrer for 30 minutes at 25°C. Then the gel was

aged at 100°C for different times (4, 8, 12, 16, 24, and 32 h). The second step was preparation of the feed stock gel ($6.5Na_2O: 2Al_2O_3: 60SiO_2: 1916H_2O$) by dissolving the alumina source as sodium aluminate ($NaAlO_2$ Sigma–Aldrich) in caustic solution then Ludox was added to the mixture and stirred for 1 h at 25°C. Then 3.2 g of the aged seed gel was added to a feedstock and stirred for 30 minutes. The overall gel was then poured in a PTFE-lined autoclave, and heated at 175°C for different crystallization time ½,1, 2, 3, 4, and 5 days. Samples had been collected from the reaction synthesis gel at different times and were analyzed. The ZSM-5 then was washed with de-ionized water until pH reached to 8 and then all samples were filtered and dried at 100°C.

3. CHRACTERIZATION

Collected synthesis gel samples were analyzed by a pH meter (Fisher Co.) at 25°C. These gel samples were characterized further by a viscometer (Haaka Co). The data of X-ray powder diffraction (XRD) for zeolite powder was collected by a Philips X' Pert PRO X–ray instrument. The Philips X' Pert PRO was set at 35.4 kV and 28 mA, CuKα (λ = 1.5418 Å) with a scanning speed of 2θ = 5-50 $^{\circ}$ min^{-1}. The synthesized samples degree of crystallization was analyzed according the same procedure mentation in **Alrubaye, 2014,** (expect the intensities of the distinguished peak where chosen for the ZSM-5 zeolite to be at 2θ =7.9°, 8.8°, 14.8°, 23.9° and 24.4°). Scanning electron microscopy (SEM) was used to identify the size and morphology of ZSM-5 crystals. Energy Dispersive Spectrometry EDS (Quanta200 FEI using Genesis software) was used to determined the Si/Al bulk ratio of zeolite samples.

4. RESULTS AND DISCUSSIN

4.1 Crystallization Time Influence on ZSM-5 Zeolite

The influence of the crystallization time on the zeolite structure and degree of crystallinity were examined using XRD analysis **Fig.1**. It was clear that by increasing the crystallization time from 1/2 to 5 days for constant ageing time of 16 h caused an increase in the crystalline phase materials until it reaches a maximum value then turns on to diminish. There was no effect of the crystallization time on purity of ZSM-5 phase however; the crystalline phase is hardly distinguished within twelve hours.

Fig.2 shows the degree of the crystallinity for the ZSM-5 at different crystallization time, which was represented by crystallinity S-shaped curves. The degree of crystallinity reaches (99.4%) after 48 h, with a pure crystalline phase of ZSM-5 and with no amorphous materials. However, the peaks intensities of the samples tend to decrease with extending the crystallization time above 48 hours and this is due to the collapse of the zeolite structure, **Feng, 2008**.

The pH of synthesized gel samples at the induction period was dropped from 11.56 to 11.35 and through the nucleation period (between 12-24 h) remained about the same value of 11.35; the pH results are consistent with the degree of crystallinity curves results. The pH change was approximately about 0.5 during the crystallization process. These results were in a good agreement with the results of **Lowe, 1983**, that showed the degree of the crystallinity increased by increasing the pH of synthesized gel and reaches to a pH of 11.8. Therefor, the pH change could be an indicator for the zeolite crystallization progressing. The same behavior as that of the pH had been

observed by measuring the viscosity of the synthesized gel as shown in **Fig.3**.

Fig.4 illustrates series of morphology of ZSM-5 at different crystallization times 1/2, 1, 2, 3, 4, and 5 days by SEM. **Fig.4a** shows tiny particles starting to form as the crystallization time elapses to ½ day. Further, when the crystallization time passes one day, changing in ZSM-5 crystal morphology was noticeable. The SEM images of the samples establish the size of the crystal of the ZSM-5 with a spherical shape **Fig.5**. By increasing the crystallization time from 1- 4 days, no significant changes in the crystal size (2.71-2.87 µm) were observed. However, by extending the crystallization time to 5 days the average crystal size was 5.71 µm.

Moreover, the EDX and the Si/Al ratio were summarized in **Table 1**. The Si/Al bulk ratio were slightly changed from 10.57 after 1 day to 10.77 after 2 days and then dropped gradually to the 10.64 after 4 days before it reached 11.17 at 5 days and that was corresponding well with the results of XRD. The crystals size was shrinking by increasing the Si/Al bulk ratio. By increasing the Si/Al weight ratio in zeolite, the crystal size became smaller, **Armaroli, 2006**, however, after 5 days the reverse behavior was observed, where the large crystals size were observed (5.71 µm for 11.17 of Si/Al ratio) due to merging between small crystals.

A comparison between the estimated degrees of crystallinity of the ZSM-5 obtained by changing the crystallization times under hydrothermal conditions revealed that a 2 days crystallization time gives smaller crystals and higher degree of crystallinity compared to prolonging the crystallization time. Therefor, 2 days crystallization time sample was chosen for its high degree of crystallinity and small crystal size to study the effect of ageing time on ZSM-5 zeolite.

4.2 Aging Time Influence on ZSM-5 Zeolite

The ageing time could have good improving on the nucleation by forming of aluminosilicate in the induction period. Improving nucleation could shorten the crystallization time and tailoring the crystal size and distribution of particle size, **Wu, 2008**. Synthesized gel was aged at 100°C at different times and synthesized under hydrothermal condition for 48 h. According to diffractograms results in **Table 2** obtained for the ZSM-5 synthesized zeolites at 4, 8, 12, 24 and 32 h hours, a crystalline phase can be observed with MFI group characteristic peak ($2\theta = 7-9^{\circ}$ and $23-25^{\circ}$). There was no secondary phase when compared with the standard zeolite, **Treacy, 2001**. From the table it is clear that the ZSM-5 samples aged for 4, 8, 12, 24 and 32 hours showed increasing of the degree of crystallinity with prolonging ageing time. The 16 h ageing time showed significant rise up to crystallinity degree to 95. The intensities for the main peaks of ZSM-5 were found to increase gradually with extending ageing time until reaching 100 % of crystallinity at 24 h ageing time then dropped to 92% at 32 h.

SEM images of ZSM-5 synthesized zeolite with different ageing times showed twined spheroidal ZSM-5 crystals as in **Fig.6**. The crystals sizes were decreasing with extending ageing time until they reached to 2.8 µm at 16 hours and then rose to 5 µm for prolonging ageing time, **Fig.7**. Moreover, the Si/Al bulk ratio was increased from 9.25 at 4 h to 10.77 at 16 h then dropped to 10.27 at 24 h and remained constant with further prolonging of the time to 32 h. These results are in good agreement with a previous work with zeolite Y, **Alrubaye, 2016**, which showed the crystal size was the minimum at long ageing time due to the formation of proper precursors which accelerate the nucleation toward zeolite.

The ageing process was beneficial to the synthesis of ZSM-5 zeolite, and could improve the induction period for nucleation formation of aluminosilicate gel. Moreover, it could also shorten the crystallization time and adjust the crystal size as well as the particle size distribution, **Wu, 2008**. **Fig.8** illustrates the effect of ageing time on crystal size and Si/Al ratio. Extending ageing time to 16 h improved the degree of crystallinity from 39 % to 95 % clearly along with shrinking in the size of crystals.

Controlling prolonging of the ageing time could eliminate the negative effect for the degree of crystallinity. However, extending the ageing time would reflect on the size and morphology of the crystals. The suitable ageing time was 24 h, and the degree of crystallinity reached up to 100% when hydrothermal synthesis conducted at 175ºC for 48 h.

5. CONCLUSIONS

ZSM-5 zeolites were synthesized successfully under hydrothermal condition. It was found that by changing the crystallization, the degrees of crystallinity increased until it reached to the optimum then dropped due to the framework collapse. The 2 days crystallization time was chosen for its high degree of crystallinity and small crystal size. The degree of the crystallinity increased by increasing the pH of synthesized gel and reached to a pH of 11.8. Therefore, the pH and viscosity changing of synthesized gel can be used as indicator for the zeolite crystallization progressing.

The prolonging ageing time of the synthesized gel resulted in increasing of the degree of the crystallinity. It was shown that the ageing time changing obviously promoted the crystallinity formation of ZSM-5 zeolites by enhancing the rate of nucleation and that was reflecting on reducing crystal size. Also, it was demonstrated that morphology of ZSM-5 obtained after different ageing times and unchanged crystallization time. Adjusting the ageing time could control the crystal size. At 24 h ageing time, the crystal size was around 2.8 μm. The suitable ageing time was 24 h, and the degree of crystallinity reached 100% through conducting the hydrothermal synthesis at 175°C for 48 h.
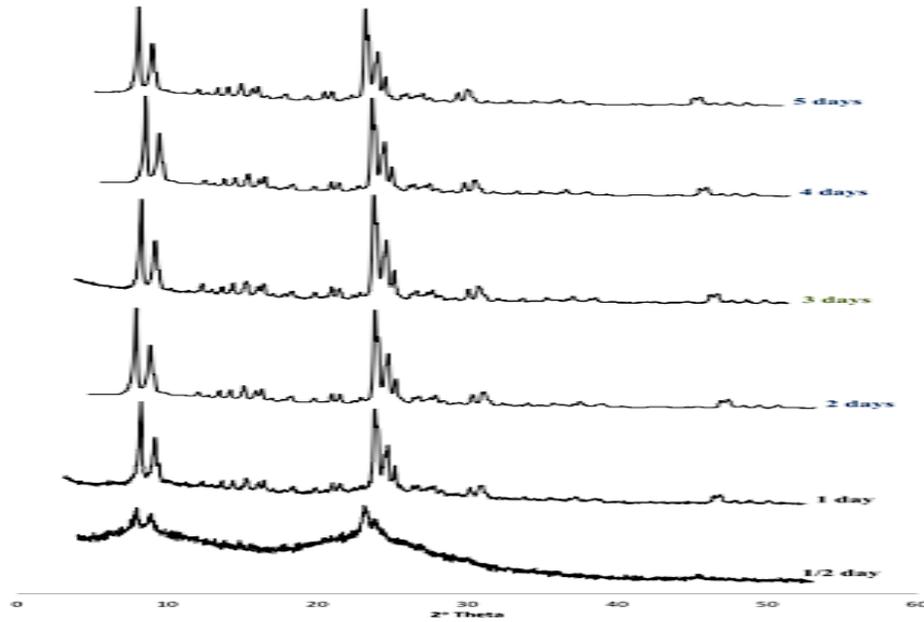
Figure 1. XRD patterns for the ZSM-5 zeolites at different crystallization times.
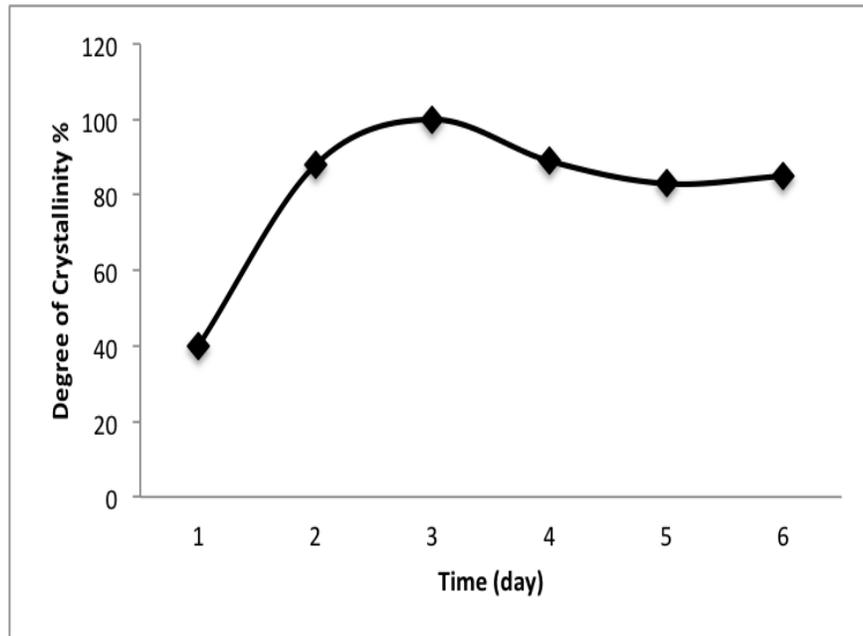
Figure 2. Crystallization times effect on the degree of the crystallinity for the ZSM-5.
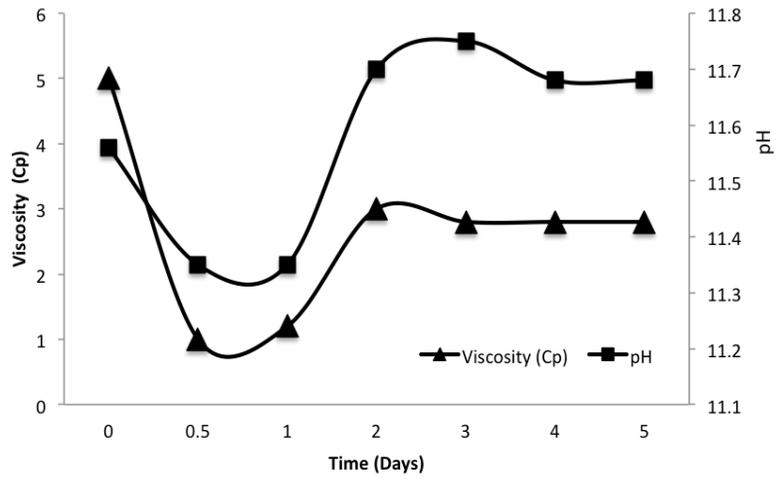
Figure 3. pH and viscosity variation of the reaction gel with the crystallisation time.
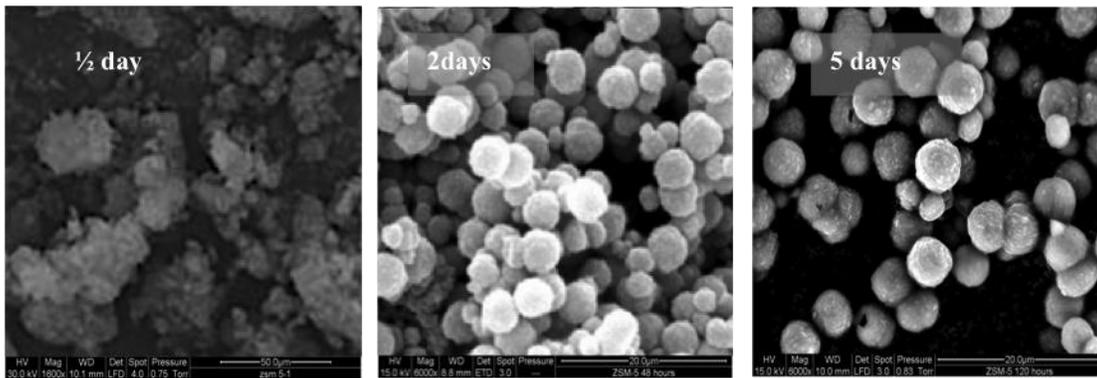
Figure 4. ZSM-5 morphology at different crystallization times.
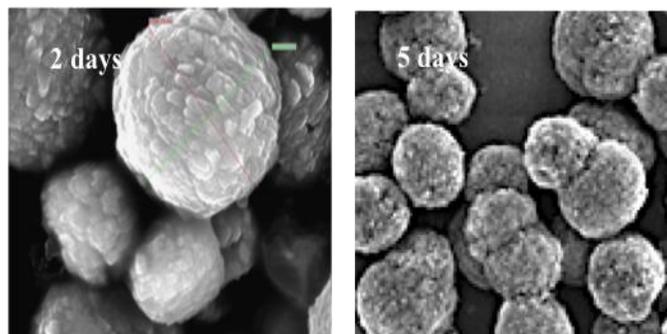
Figure 5. `ZSM-5 crystal size at different crystallization times.

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Table 1. Effect of crystallization time on Crystal size, Si/Al molar ratio, crystallinity.

ZSM-5 samples	½ day	1 day	2 days	3 days	4 days	5 days
Degree of Crsytallinity (%)	40	88	94	89	83	85
Si/Al Bulk ratio	/	10.57	10.77	10.70	10.64	11.17
Crsytal size (µm)	/	2.97	2.47	2.71	2.87	5.71

Table 2. XRD for different ageing time synthesized ZSM-5 zeolites.

Standard MFI		Different ageing times ZSM-5 samples					
2θ	I_{rel}	I_{rel} 4h	I_{rel} 8h	I_{rel} 12h	I_{rel} 16	I_{rel} 24	I_{rel} 32
7.93	10.59	2.26	4.49	4.45	10.53	10.59	14.65
8.9	6.97	1.75	3.27	3.02	6.95	6.97	8.81
11.99	1.86	0.84	0.9	1.06	1.96	1.86	1.24
13.25	1.97	0.84	0.79	0.91	1.49	1.97	1.57
13.96	2.16	0.93	0.74	1.12	1.99	2.16	1.94
14.61	2.52	0.75	1.08	0.96	2.45	2.52	2.68
15.63	1.90	0.77	1.26	1.07	2.37	1.90	1.69
15.92	2.12	0.69	1.01	0.93	1.86	2.12	2.09
16.66	1.59	0.68	0.57	0.95	2.18	1.59	1.07
17.32	1.23	0.59	0.5	0.62	1.16	1.23	0.87
17.64	1.32	0.57	0.54	0.53	1.32	1.32	1.34
19.24	1.06	0.62	0.65	0.47	1.12	1.06	1.08
20.37	1.52	0.79	0.8	0.63	1.68	1.52	1.24
20.92	1.6	0.68	0.45	0.7	1.68	1.6	1.57
22.20	1.18	0.59	0.56	0.61	1.14	1.18	1.00
23.10	10.53	3.61	5.18	5.01	10.68	10.53	8.24
23.98	6.25	2.59	3.15	3.06	6.55	6.25	4.20
24.61	3.94	1.74	1.91	1.47	3.37	3.94	2.80
25.54	1.78	0.77	0.55	0.73	1.27	1.78	0.96
25.85	1.44	0.62	0.79	0.58	1.37	1.44	1.23
26.91	1.44	0.71	0.7	0.61	1.44	1.44	1.25
27.44	1.24	0.88	0.39	0.72	1.30	1.24	0.76
28.14	1.06	0.51	0.64	0.63	0.96	1.06	0.60
28.42	0.96	0.55	0.9	0.41	1.30	0.96	0.66
29.22	1.71	0.84	0.47	0.69	1.46	1.71	1.17
29.94	1.90	0.59	0.32	0.97	1.89	1.90	1.42
30.28	1.16	0.55	0.34	0.38	0.59	1.16	0.96
32.74	0.57	0.84	0.33	0.32	0.65	0.57	0.68
34.34	0.59	0.57	0.33	0.35	0.75	0.59	0.78
35.72	0.64	0.37	0.3	0.28	0.69	0.64	0.70
37.63	0.66	0.34	0.28	0.31	0.98	0.66	0.56
45.14	1.06	0.35	0.32	0.26	1.14	1.06	1.00
45.64	1.01	0.31	0.62	0.37	1.06	1.01	1.02
46.50	0.63	0.2	0.24	0.48	0.51	0.63	0.44
47.48	0.62	0.24	0.17	0.27	0.53	0.62	0.46
48.59	0.50	0.23	0.19	0.29	0.51	0.50	0.47
Σ	80.51	31.43	36.34	36.99	79.18	80.51	74.51
Degree of crystallinity	100	39	44	46	95	100	92
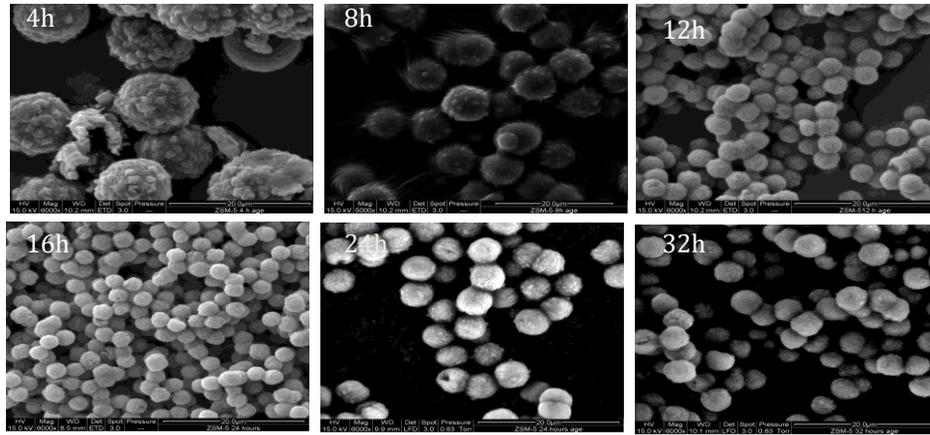
Figure 6. SEM images of ZSM-5 for different ageing times.
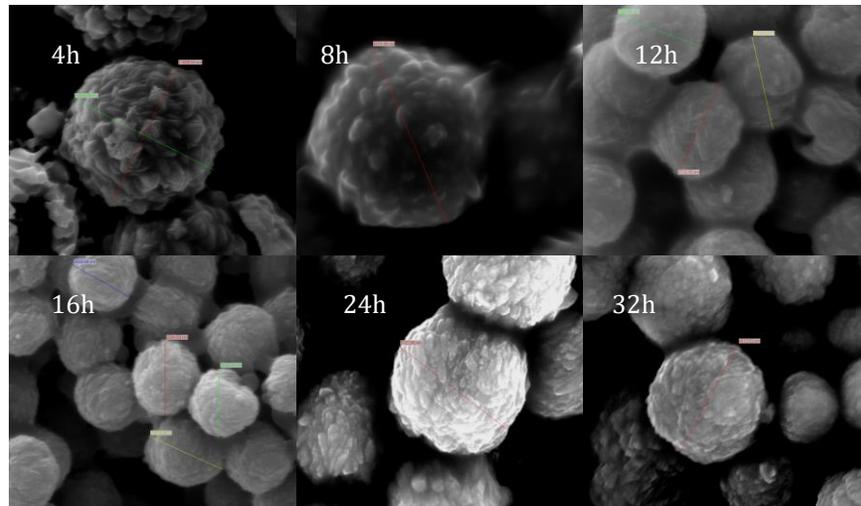
Figure 7. ZSM-5 crystal size at different ageing times.
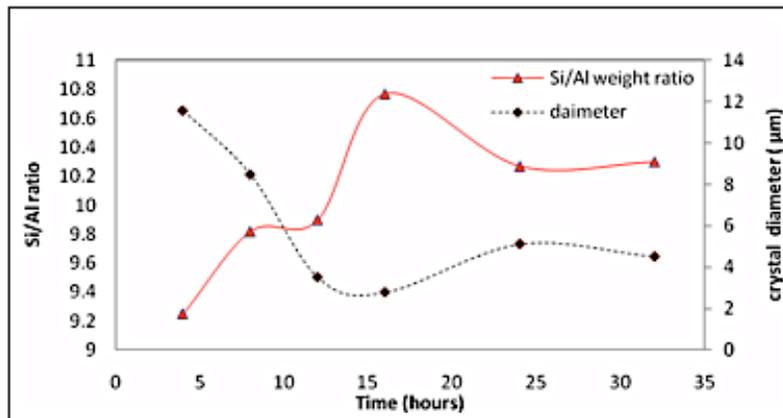
Figure 8. Effect of ageing time on the crystal size, Si/Al bulk ratio.

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