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Accelerated Synthesis of Deca-Dodecasil 3 Rhombohedral (DDR3) Zeolite Crystals via Hydrothermal Growth Coupled with Ultrasonic Irradiation Method

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Abstract - In the present work, DDR3 zeolite crystals were synthesized via hydrothermal heating coupled with ultrasonic irradiation method. The durations of hydrothermal heating were varied from 0.5-10 days and the temperature was maintained at 160^{o}C. Meanwhile, the durations of ultrasonic irradiation were varied from 1 h to 3 h. The crystallinity, surface morphology and bond vibration of the resultant samples were characterized using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and Fourier transform infrared spectroscopy (FTIR), respectively. The XRD results showed that the peaks representing DDR3 structure were obtained for the sample synthesized in 10 days with ultrasonic irradiation of 3 h. XRD peaks of the sample synthesized in 5 days with ultrasonic irradiation of 2 h also demonstrated the structure of DDR3 topology. Samples synthesized in 1, 2 and 5 days with ultrasonic irradiation of 1 h also demonstrated the structure of DDR3 topology. However, the sample synthesized in 0.5 day with 1 h of ultrasonic irradiation didn't showed DDR3 topology due to absence of major peaks in XRD pattern. For comparison purpose, reference DDR3 crystals were synthesized in 25 days without ultrasonic irradiation. From these results, it can be concluded that conventional hydrothermal heating coupled

with ultrasonic irradiation has successfully reduced the synthesis duration of DDR3 zeolite from 25 days to 1 day.

Key words; DDR3 zeolite Crystals, Synthesis, ultrasonic irradiation

1. Introduction

The research on zeolites has been started since last century when they were first found by the Swedish mineralogist Cronsted in 1756 [1], while Weigel and Steinhoff introduced the use of zeolites as molecular sieves in 1925 [2]. Zeolites are inorganic microporous crystalline materials having well defined apertures of uniform molecular dimensions. Zeolites consist of tetrahedral structure in which a small silicon or aluminum ion is surrounded by four oxygen anions. Three-dimensional arrangement is formed when silica and alumina tetrahedral link to each other by the sharing of their corners. Zeolites are classified into three categories i-e large pores (FAU, MOR), medium pores (MFI, MEL, FER) and small pores (LTA, CHA, DDR) [3]. Due to their excellent properties such as stable in high thermal, chemical, mechanical and pressure stability [4], zeolites have been extensively used in the petrochemical-related industries including catalysis, adsorption and separation processes [5].

DDR3 is a pure silica small pore zeolite with a chemical formula of $(C_{10}H_{17}N)_6(N_2)_9(Si_{120}O_{240})$. DDR3 contains crystal structure of 4, 5, 6, and 8 Si atoms in rings [6] and three different building blocks (cages) namely decade hadron, dodeca hadron cages and hadron cage. Among all cages in DDR3, only 8 - ring window has opening through which it is accessible [7]. The hydrophobic and molecular-sieving property of DDR3 have resulted it as a suitable candidate not only in CO_2 separation but also in

olefin/paraffin mixture separation [8]. Figure 1 shows building blocks and framework of DDR3 zeolite crystals [7].

In 1986, Gies. H [9] firstly introduced the synthesis of DDR3 zeolite crystals. In 1994, den Exter et al. [7] reported the optimization study on the synthesis duration, water concentration and conventional heating temperature for obtaining DDR3 zeolite crystals. They successfully synthesized DDR3 crystals in 25 days at 160 °C using tetramethoxysilane (TMOS) as a silica source. Subsequently, Tomita et al. 2004 [10] reported the synthesis of DDR3 zeolite particles following the method reported by den Exter et al. [7]. In 2007, Alves [11] studied the effect of water concentration, pH, aging time and temperature on the synthesis of DDR3 crystals. In 2009, Qi-Liang et al. [12] synthesized DDR3 crystals in 9 days using fluoride medium. Gucuyener et al. 2011 [6] studied the effect of mineralizing agent KF and autoclave cleaning on the synthesis of DDR3 crystals. They successfully synthesized DDR3 crystals in 1 day using DDR3 seeds prepared by using den Exter et al. [7] method. In 2014, Mitali Sen et al. [13] successfully synthesized DDR3 crystals in 5 days at room temperature by applying ultrasonic irradiation on the synthesis solution for 3h and Ludox-40 as silica source prior to the crystallization of DDR3 particles.

As reported in the literature, DDR3 crystals required very long synthesis duration, as it consumed 25 days using conventional heating method. Researchers are yet to focus on DDR3 crystals because of long synthesis time constraints. The ways to reduce the synthesis duration of DDR3 crystals still remain a challenging issue. Therefore, a facile method to reduce the synthesis duration of DDR3 crystal is very crucial due to its promising characteristic for industrial application. Ultrasonic irradiation and microwave assisted hydrothermal synthesis are relatively new techniques for synthesizing inorganic

materials like zeolites and ceramics [14, 15]. Although microwave assisted hydrothermal heating method has been successfully applied for the synthesis of zeolites (ZSM-5, silicate-1 and ZSM-22) [15-18] and metal-organic frameworks [15] with the reduction of synthesis duration, is more expensive compared to ultrasonic irradiation method. In the present work, we introduced ultrasonic irradiation for the synthesis of DDR3 crystals, as an initial stage for the investigation of possible reduction in the synthesis duration of DDR3 crystals. Ultrasonic irradiation is considered as a potential technique for the synthesis of inorganic materials due to its ability to generate homogeneous nucleation and influence the crystallization kinetics [19]. The ultrasound waves create high energy cavitation which can accelerate the reaction duration between solids present in the liquids [20]. Besides, according to Enomoto et al. (1997) ultrasonic irradiation method required low temperature and less crystallization time as compared to hydrothermal heating method [21]. Therefore, ultrasonic irradiation has attracted increasing interest in the synthesis of inorganic materials like zeolites [22]. Various researchers had successfully reduced the synthesis duration of zeolites like; i-e MCM-22, zeolite ANA, B-ZSM-5, SaPO-34, NaP, and zeolite-T using ultrasonic irradiation method.

Wu et al. (2008) reported the ultrasonic irradiation effect on zeolite MCM-22 gel. It was observed that without ultrasonic irradiation, crystallization time of MCM-22 was 120 h, while using ultrasonic irradiation method, MCM-22 can be synthesized within 48 h [23]. Subsequently, Azizi and Yousefpour (2010) studied the static and the ultrasonic irradiation effect on the synthesis of analcime (ANA zeolite) crystals. They reported that the crystallization duration of ANA zeolite can be reduced from 96 h to 48 h, using ultrasonic irradiation. They also concluded that the increase in ultrasonic irradiation can

leads to transformation of spherical ANA zeolite into rod-like ANA zeolite [24]. Meanwhile, Abrishamkaret and his coworkers found that ultrasonic irradiation could significantly reduce crystallization time of B-ZSM-5. They reported that B-ZSM-5 zeolite can be synthesized in 18 h using ultrasonic irradiation [25]. In 2012, S. Askari and R. Halladj successfully synthesized SAPO-34 zeolite within 1.5 h using ultrasonic irradiation. They also found that the SAPO-34 crystals synthesized using ultrasonic irradiation changed morphology from spherical shape to cubic shape [26]. Subsequently, Pal et al. (2013) synthesized NaP zeolite at room temperature and shorten synthesis duration using ultrasonic irradiation. They successfully reduced the synthesis duration of NaP zeolite from 24 h to 3 h [27]. Recently, Izzati et al. (2014) reported synthesis of zeolite T using ultrasonic irradiation. They successfully reduced the synthesis duration from 7 days (168 h) to 2 days (48 h) [28]. From all above successful cases, it can be concluded that ultrasonic irradiation can significantly reduce the synthesis duration of zeolites. Table 1 shows the ultrasonic irradiation and hydrothermal heating effect on the synthesis durations of zeolites reported by various researchers.

In this work, we reported the accelerated synthesis of DDR3 crystals using hydrothermal growth coupled with ultrasonic irradiation method. The resulting DDR3 crystals were characterized for its crystallinity, morphology and bond vibration using XRD, FESEM and FTIR respectively. The effect of ultrasonic irradiation on the synthesis duration, morphology and crystallinity of DDR3 crystals were studied.

2. Experimental

2.1. Chemicals and Materials

Tetramethoxysilane (Merck) was used as silica source, 1-adamantaneamine (Fisher Scientific > 96%) was used as structure directing agent, ethylenediamine (Merck) was used for maintaining pH and DI-ionized water. All chemicals and reagents were used as received.

2.2. Synthesis of DDR3 Crystals

DDR3 crystals were prepared by using conventional heating method described by den Exter et al. [7]. The solution mixture was prepared by dissolving 1.422g of 1-adamantaneamine (Fisher Scientific 96%) in 4.85g of ethylenediamine (Merck), and then 40.464g of di-ionized water was added rapidly. Subsequently, the mixture was agitated at 200 rpm for 1 h at room temperature. After heating the mixture for 1 h at 95 ºC with continuous agitation, it was cooled down with ice for 20 min. Then, 3.044 g of tetramethoxysilane (Merck) was added drop by drop in ice cooled mixture. After that, the mixture was again heated for 3 h at 95 ºC with continuous agitation. The molar ratio of the final mixture solution was 1-adamantaneamine: Silica: Ethylenediamine: Water = 47:100:404:11,240. In the present work, seven samples were synthesized using the same solution mixture, with different ultrasonic irradiation and hydrothermal heating durations. For comparison purposes, Sample 1 as reference sample was synthesized by using conventional hydrothermal heating method at 160 ^{o}C, as described by den Exter et al. [7], without ultrasonic irradiation. Sample 2 was prepared by using the same solution mixture irradiated by ultrasound for 3 h and heated in the pressure vessel for hydrothermal growth for 10 days at 160 ºC. In order to study the effect of ultrasonic irradiation duration on the development of DD3R zeolite crystals, the solution mixture was underwent ultrasonic irradiation for 2 h and then, heated in pressure vessel for hydrothermal growth for 5 days at 160 ºC and coded as Sample 3. The solution mixture

used to synthesis of samples 4 – 7 were underwent ultrasonic irradiation of 1 h prior to hydrothermal heating. Subsequently, these solution mixtures were heated in the pressure vessel for hydrothermal growth for 5 days, 2 days, 1 day and 0.5 day at 160 ºC, respectively. All the powder products were recovered by using centrifugation and repeated washed with de-ionized water followed by drying overnight at 100 ºC. Table 2 shows the samples synthesized in the present work using various conditions.

The resulting crystals were characterized for its crystallinity, morphology and bond structure using XRD, FESEM and FTIR, respectively. XRD was carried out on Philips 1710 diffractometer using CuK*a* radiation (a = 1.541 A°) in the 2theta range of 5–35° at ambient temperature. Morphology of DDR3 crystals was measured in field emission scanning electron microscopy (FESEM Model: Zeiss Supra 55 VP). The bond structure for DDR3 crystals were examined by FTIR using KBr pellet method (FTIR Model: Pelkin Elmer, Spectrum one).

Results and Discussion

3.1 X-ray Diffraction (XRD)

Figure 2 shows the XRD patterns of samples 1-7 synthesized in the present work. The XRD pattern obtained for the reference sample synthesized in 25 days without ultrasonic irradiation showed all the major peaks of DD3R structure at 2θ values of 9 º, 17 º, 18 º, 19 º, 19.5 º and 20 º. These significant peaks at 2θ values are consistent with those peaks reported in the literature for DDR3 structure [10]. Referring to Figure 2, the presence of peaks in the XRD pattern of samples 2-6 confirmed the crystalline structure of DDR3. However, sample 7 shows the mixture of amorphous and crystalline phases due to the absence of major peaks at 2theta values from 17-19º.

These results show that, ultrasonic irradiation has successfully reduced the synthesis duration of DDR3 zeolite crystals from 25 days to 1 day without affecting the crystallinity of the DDR3 crystals. Ultrasonic irradiation is not affecting the degree of crystallinity of samples 2-6 because XRD pattern of these samples showed similar peaks intensity compared with sample 1.

Suslick et al. (1990) reported the effect of ultrasonic irradiation on the solid-liquid system. They found that the evolutions of energy during the ultrasonic irradiation collapse the solution bubbles and help in the formation of free radical. This free radical stimulates the reaction species, which accelerates the nucleation and helps in crystal growth formation [29]. Therefore, similar observation can be used to explain the finding in the present work. In fact, the mechanism could be elucidated in the schematic shown in Figure 3, which was also reported by Bose et al.(2014) [30]. Referring to Figure 3, during the ultrasonic irradiation, two Si $(OH)_4$ species from silica source, come in contact to form Si–O–Si through a transition state. During the formation of Si–O–Si, high activation energy formed under ultrasonic cavitations followed by the removal of water molecules [31]. Following by the next step, Si–O–Si bond interacts with cationic organic structure directing agent to form porous structure. In the case of DDR3 synthesis, the reaction takes place under basic conditions, where the silica species are present as anions and cationic species is 1- adamantanamine (structure directing agent). The schematic of the reaction between species 1 and species 2 is described in Figure 4 [30].

From these results, it can be confirmed that crystals synthesized in 1 day at 160 $^{\circ}$C with ultrasonic irradiation for 1 h demonstrated the structure of DDR3 topology. Synthesis of DDR3 crystals in 1 day is an appreciable short duration as compared to 25 days reported in literature.

3.2 Field-Emission Scanning Electron Microscopy (FESEM)

Figure 5 shows the FESEM images of Sample 1-7. As shown in Figure 5, the DDR3 crystals synthesized in 10 and 25 days shows octahedron shape which is in coherence with those DDR3 crystal morphology reported in the literature [10]. From this observation, it can be concluded that

no morphology altered, when synthesis duration of DDR3 crystals is reduced to 10 days. Furthermore, samples 3 - 6 exhibit hexagonal morphology which is another morphology of DDR3 crystals as reported by Zhou et al. (2014) [32]. Interestingly, it can be seen that when synthesis duration of DDR3 crystals is decreasing from 10 days to 5 days, morphology of crystals is altered from octahedron to hexagonal shape. Subsequently, when synthesis duration of DDR3 crystals reduced from 5 days to 1 day, the crystals morphology of the samples remains unchanged. In addition, although sample 7 also showed the hexagonal morphology but in this case, crystals with sigma 2 phase (Fig. 2) were formed instead of DDR3, and also with the presence of amorphous phase. These changes reveal that the ultrasonic irradiation shows a vital role in the morphology control during the formation of DDR3 crystals. FESEM results of all samples are consistent with the XRD peaks shown in Figure 2.

3.3 Energy dispersive X-ray (EDX)

The concentrations of different elements presence in DDR3 crystals were measured by energy-dispersive X-ray (EDX). Figure 5 shows the normalized EDX results for all samples synthesized in the present work. According to the chemical formula of DDR3 crystals, $(C_{10}H_{17}N)_6(N_2)_9(Si_{120}O_{240})$, the Si and O elements are in major quantity. The EDX results show that the compositions of Si element presence in the samples are in the range from 35 to 39 wt%. These results are comparable with those results reported in the literature [30]. Referring to Figure 5, when the synthesis duration of the samples reduced from 25 days to 1 day, the compositions of Si element in the sample slightly decreases from 39.13 to 35.30 wt%. Meanwhile, the composition of Si element in sample 7 is 30.21 wt%. This phenomenon could be explained by the decrease in percentage yield of the crystals obtained, when the synthesis duration of the samples reduced from 25 days to 0.5 day. The decrease in the percentage yield of the crystals is mainly due to incomplete reaction between the silica source (tetramethoxysilane) and 1-adamantaneamine (structure directing

agent). From these results, it can be concluded that EDX analysis supports the XRD and FESEM observations.

3.4 Fourier Transform Infrared (FTIR)

The FTIR spectra of all samples synthesized in the present work is shown in Figure 6. The spectrum of sample 1 showed characteristic peaks at 3720 cm^{-1}, 1579 cm^{-1}, 1484 cm^{-1}, 1326cm^{-1}, 1100cm^{-1}, 788 cm^{-1}, 725cm^{-1}, 548cm^{-1} and 467cm^{-1} which are consistent with the FTIR peaks reported in the literature for DDR3 structure [13]. The characteristic peaks at 788 cm^{-1} and 467 cm^{-1} were attributed to O–Si–O and Si–O tetrahedral bonding, respectively. In addition, the appearance of the peaks at 725 cm^{-1} and 1579 cm^{-1} were assigned to the external linkage and vibration of water molecules, respectively. The peaks identified at 3720 cm^{-1}, 1484 cm^{-1}, 1326 cm^{-1} and 1100 cm^{-1} are correspond to the symmetric stretching vibration of Si-N and N-H bond. Furthermore, the vibration of internal tetrahedron was shown at 548 cm^{-1}. It can be observed that the FTIR peaks of samples 2 - 6 showed similar vibration as described in sample 1 and confirmed the formation of DDR3 topology. Interestingly, the spectrum of the sample synthesized in 0.5 days did not show the peaks as described for DDR3 topology due to the missing of the characteristic peaks at 3720 cm^{-1}, 1579 cm^{-1}, 1484 cm^{-1} and 1326 cm^{-1}. The FTIR results were in agreement with the XRD and FESEM results.

3. Conclusions

In this work, we concluded that ultrasonic irradiation coupled with a conventional hydrothermal heating method has successfully reduced the synthesis duration of DDR3 zeolite crystals from 25 days to 1 day. This was mainly due to the ultrasonic energy produce the free radicals which helps for rapid nucleation and crystallization of zeolite materials. XRD, FESEM and FTIR analysis confirmed the formation of DDR3 crystals. The successful reduction of the synthesis duration of

DDR3 crystals could result in the significant reduction of the synthesis duration for DDR3 zeolite membrane in the future work.

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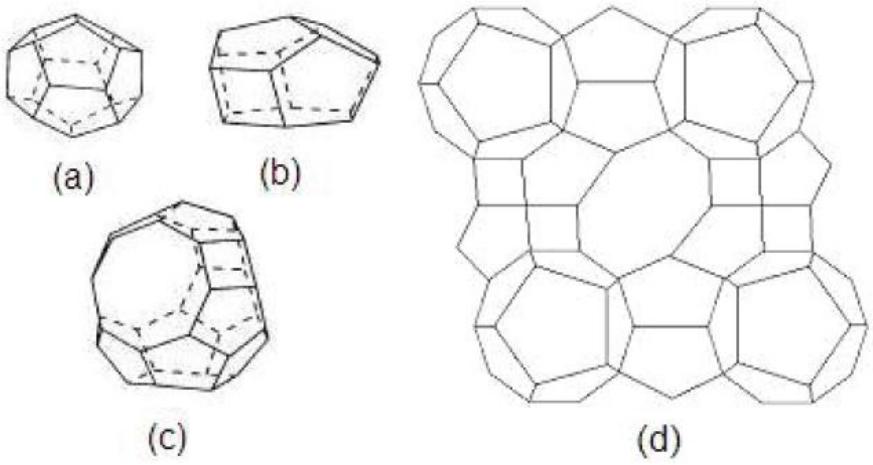


Fig.1. Building blocks and framework of DDR3 zeolite crystals [7].

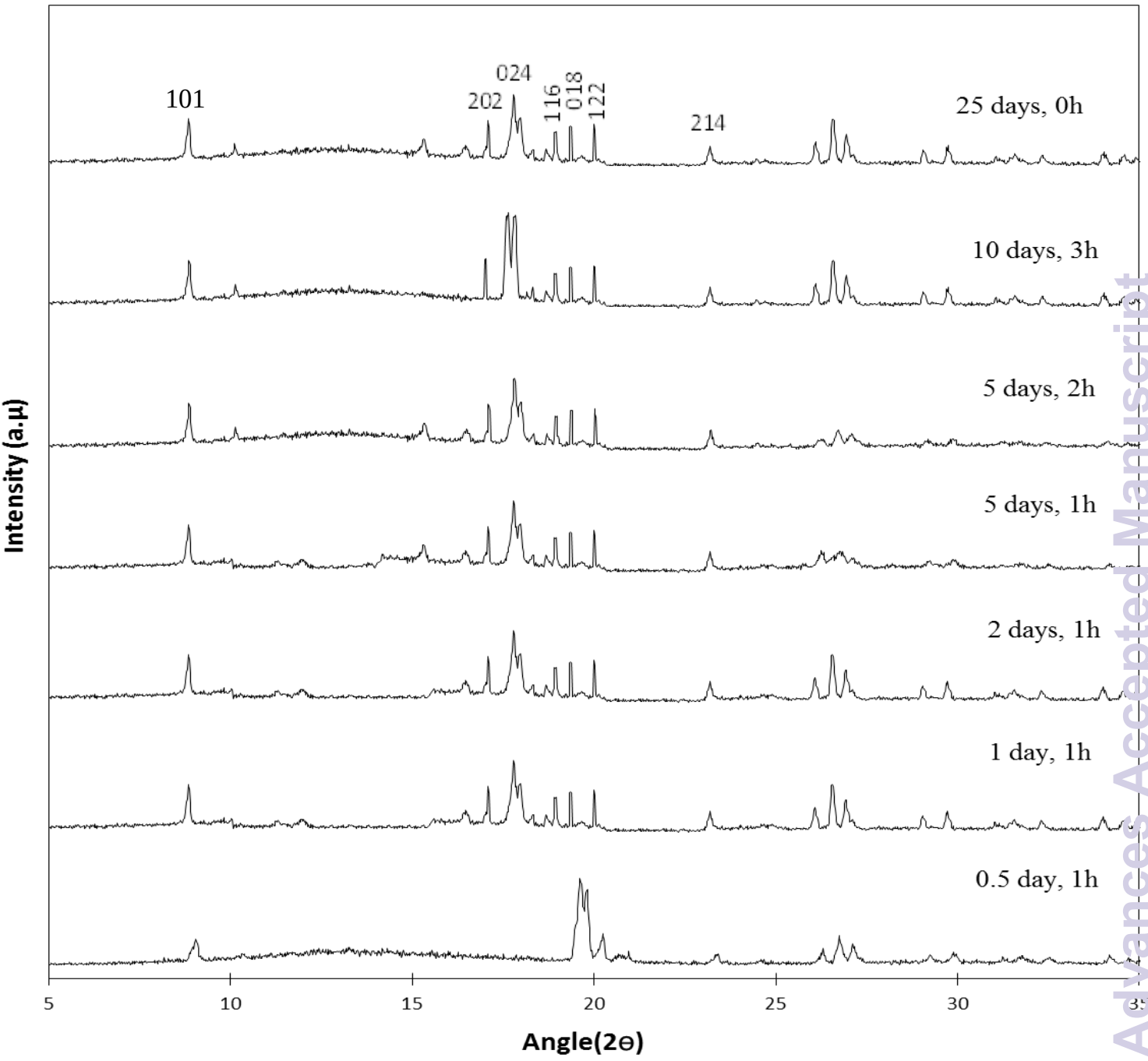


Fig.2. XRD pattern of all samples synthesized in the present work.

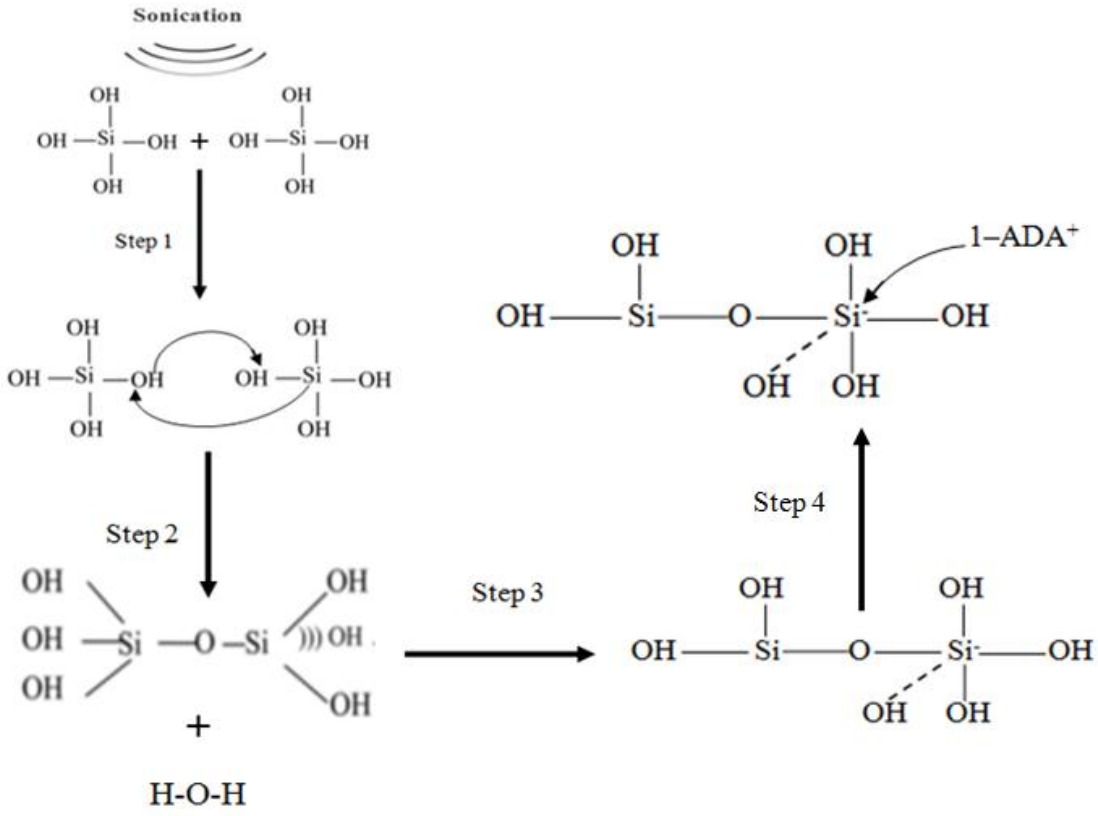


Fig.3. Schematic of reaction mechanism between two silica atoms [30].

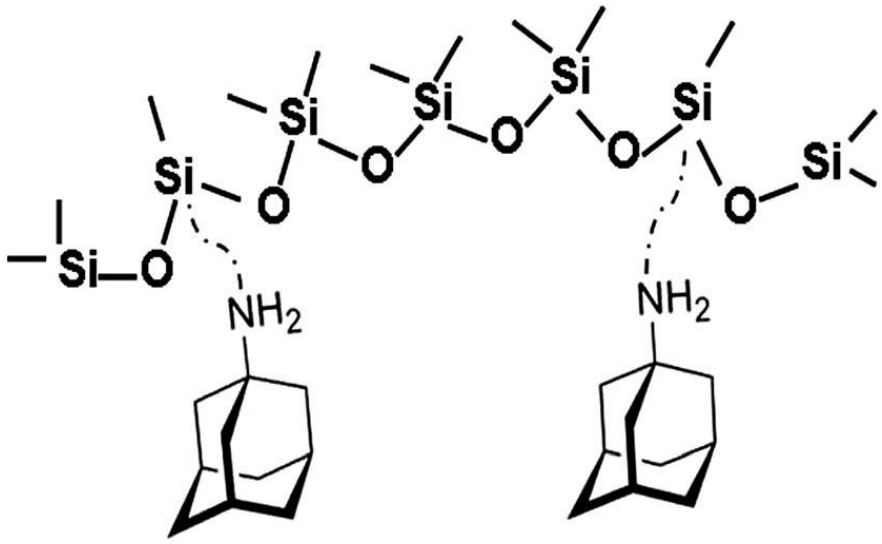
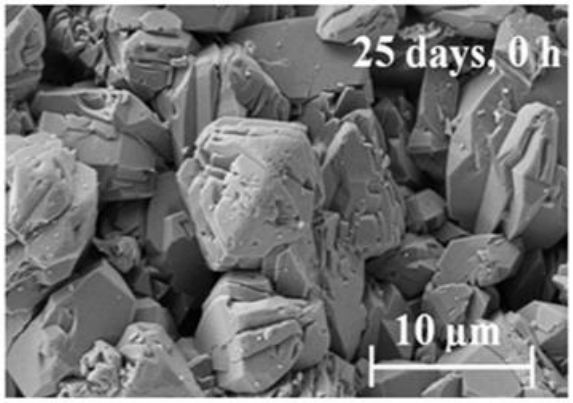
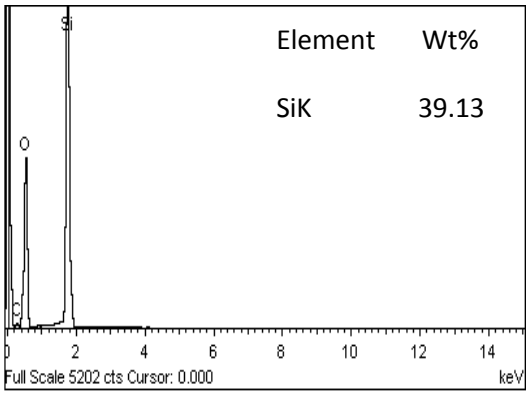
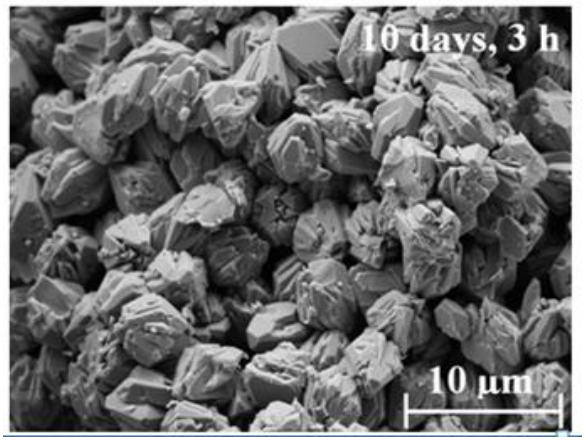
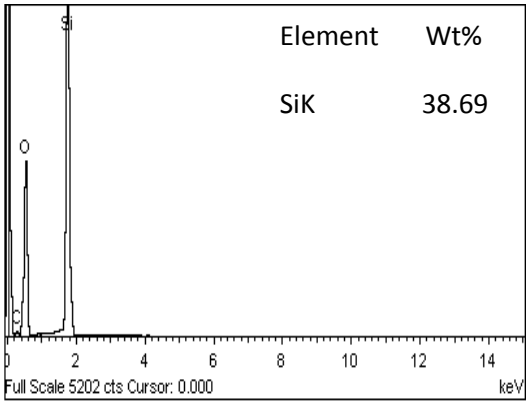


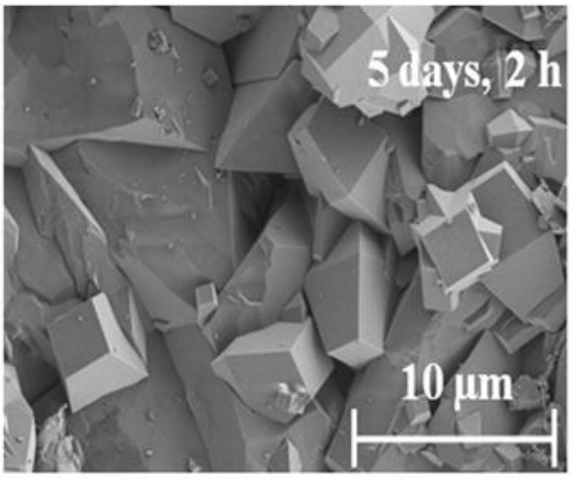
Fig.4. Schematic of reaction between silica and 1-adamantanamine [30].

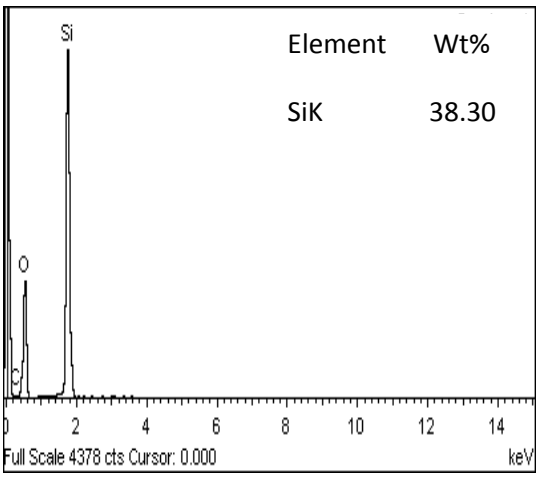


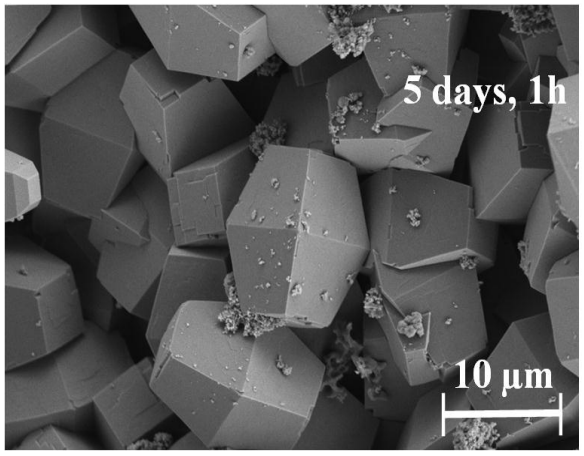


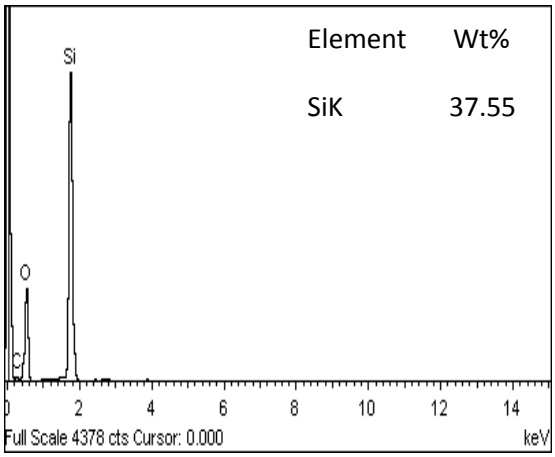












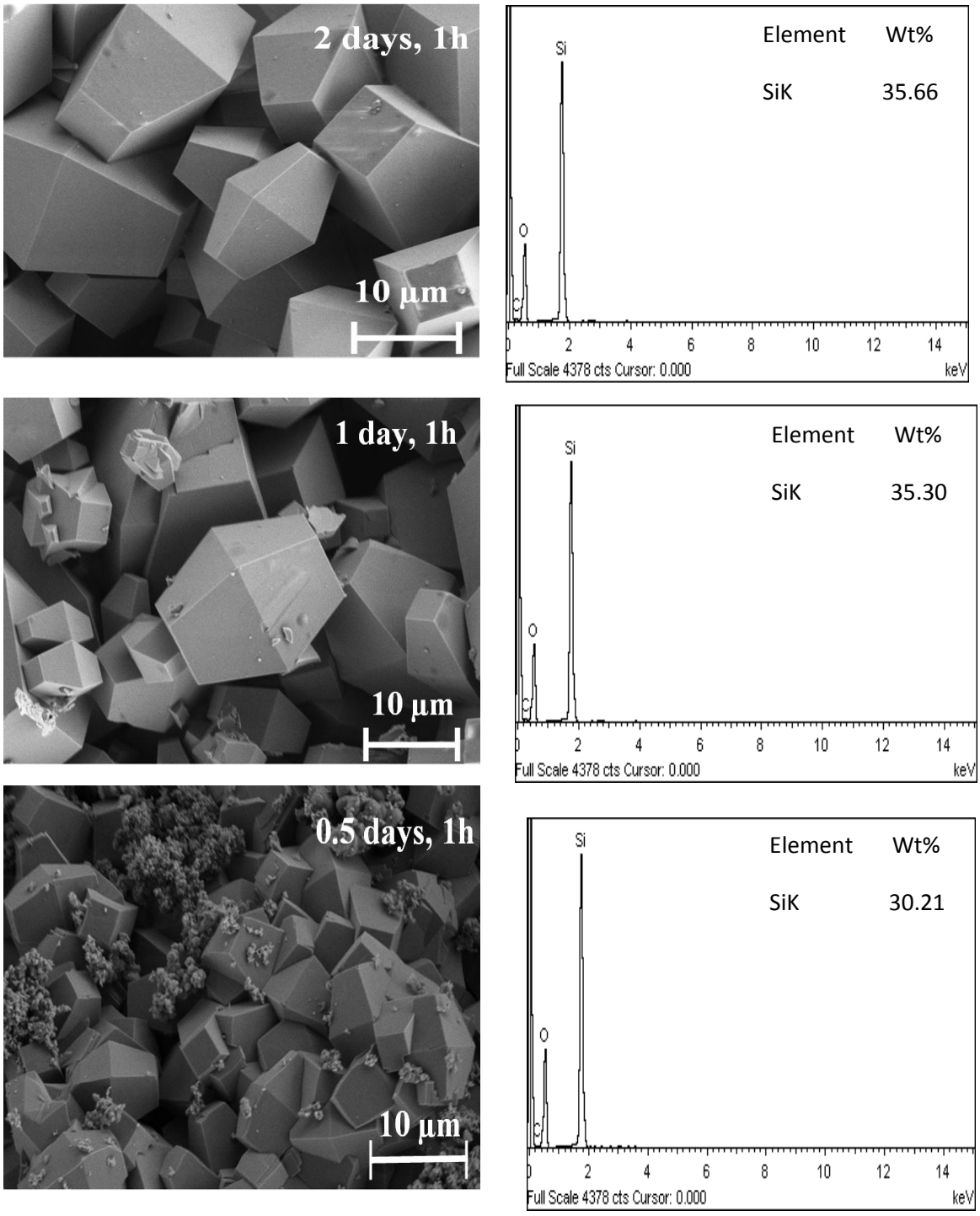


Fig.5. FESEM micrographs and corresponding EDX analysis of all samples synthesized in the present work.

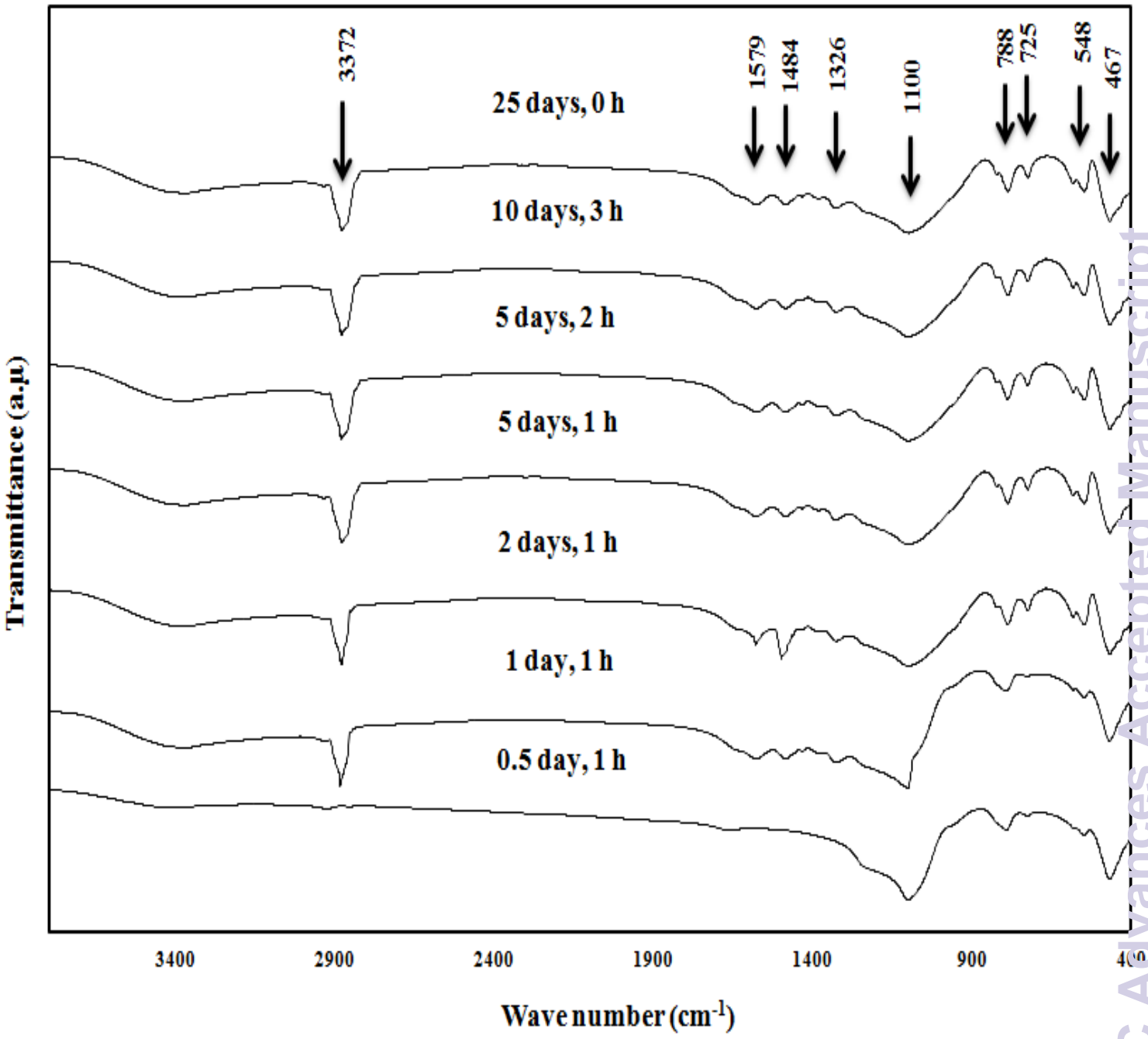


Fig.6. FTIR spectra of all samples synthesized in the present work.

Table 1: Effect of ultrasonic irradiation on the synthesis of zeolites reported by various researchers

Material	Synthesis duration (h) using ultrasonic irradiation coupled with hydrothermal heating	Synthesis duration (h) using hydrothermal heating	References
MCM-22	48	120	[23]
Zeolite ANA	48	96	[24]
B-ZSM-5	18	120	[25]
SAPO-34	1.5	24	[26]
NaP	3	24	[27]
Zeolite – T	48	168	[28]

Table 2: DDR3 crystals synthesized in the present work using ultrasonic irradiation coupled with conventional hydrothermal heating method.

Samples	Ultrasonic irradiation (h)	Conventional Hydrothermal heating (days)	Structure
Sample 1	-	25	DDR3
Sample 2	3	10	DDR3
Sample 3	2	5	DDR3
Sample 4	1	5	DDR3
Sample 5	1	2	DDR3
Sample 6	1	1	DDR3
Sample 7	1	0.5	Amorphous +Sigma 2