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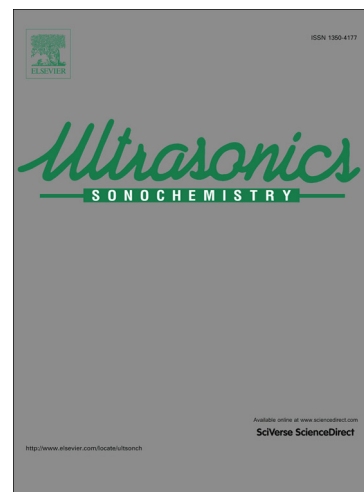Please cite this article as: D. Reinoso, M. Adrover, M. Pedernera, Green synthesis of nanocrystalline faujasite zeolite, *Ultrasonics Sonochemistry* (2017), doi: https://doi.org/10.1016/j.ultsonch.2017.11.034

GREEN SYNTHESIS OF NANOCRYSTALLINE

FAUJASITE ZEOLITE

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ABSTRACT

In this work, the synthesis of 28 and 38 nm Na-Y zeolite nanocrystals is reported. The process was performed via green synthesis without any organic structure directing agents (SDAs), at low temperature and applying ultrasound-assisted aging. The zeolite nanoparticles obtained were characterized by X ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N_2 adsorption - desorption isotherm at 77K. A simple, fast, efficient and environmentally friendly procedure to synthetize nanocrystalline FAU zeolite is described in the present study. The sonochemical pretreatment was found to directly affect the Na-Y zeolite properties. The final product obtained via ultrasound pretreatment shows high phase purity and crystallinity degree with crystal size smaller than 38 nm and elevated surface area (S_{BET} ~950 m^2g^{-1}). The hierarchical micro- and mesoporous FAU zeolites exhibit a pore volume of ~0.4 cm^3g^{-1}.

1. INTRODUCTION

Zeolites are widely used as catalysts or catalyst supports in a variety of applications in refining and (petro)chemical industries [1]. Particularly, the faujasite type framework (FAU), is an aluminosilicate with cavities of 1.3 nm of diameter interconnected by pores of 0.74 nm. Depending on the Si/Al molar ratio, faujasite zeolites can be subdivided into X-type (Si/Al=1.0-1.5) and Y-type (Si/Al>1.5) [2]. This FAU-type zeolite is widely used in industrial processes, for instance, in the fluid catalytic cracking (FCC), and adsorption of volatile organic compounds in the gas streams [3].

Recently, the development of zeolites synthesis methods to reduce the size of the particles has received special interest. Micrometer sized zeolites have a negligible external surface area compared with the large surface area in their internal microporous. However, some catalytic reactions occur on the external surface which usually is smaller in relation to the reactions that take place inside microporous [4]. Nanoparticles zeolites lead to substantial changes in the material properties increasing the intercrystalline space, the external and internal surface area and volume and pore mouths exposed. Therefore, the application of nanozeolites in some catalytic reactions can reduce diffusion path lengths and increase catalytic activity and selectivity, as well as improve reaction medium stability [5,6,7].

Na-Y zeolite nanoparticles synthesis using different methods based primarily on strategic control of the hydrothermal process conditions have been previously reported [8-11]. Many nanocrystal zeolites synthesis procedures involve the use of organic templates to direct the formation of a targeted zeolite phase. However, most organic templates used are corrosive and toxic, besides

the high calcination temperature required to remove them that leads to large energy consumption as well as the generation of harmful and pollutant volatile organic compounds. Moreover, most organic templates are very expensive which could increase zeolites production costs [12].

Environmentally friendly synthesis methodologies involve not only the use of green starting reagents, in other words, non-toxic, inexpensive and abundant reagents but also environmentally benign synthesis conditions such as low temperature hydrothermal synthesis, microwave or ultrasound-assisted synthesis [4]. The most common green synthesis is organic template free via transformation of natural source, seeded growth approach and multi-step strategy [4]. The FAU nanocrystalline synthesis in the absence of organic template has been explored [13-21].

Additionally, sonochemical synthesis by ultrasonic irradiation is a new method for synthesis of nanoparticles in catalysis [22]. This method is simple, fast and does not need complicated facilities. In zeolite synthesis procedures, ultrasound treatment impacts on the nucleation and crystal growth processes, resulting both in shorter crystallization time and induction period and different effect on morphology and particle size [23-26]. The driving force for sonocrystallization is acoustic cavitation. The above phenomenon generates high energy that facilitates the formation of radicals responsible for the primary nucleation and crystal growth in a crystallization process [27].

This study reports a green synthesis procedure through the strategic combination of synthesis parameters and the use of ultrasound to assist the aging stage to obtain hierarchical FAU zeolite with uniform nano- sized crystals. The synthesis methods proposed to obtain FAU structure with highly desirable

properties were simple, fast and efficient organic free procedures. Also, the sonication pretreatment effect on crystallinity, particle size, morphology and textural property were evaluated.

2.   EXPERIMENTAL

2.1.   Material and methods

The reagents used for the Na-Y zeolite synthesis were sodium hydroxide (99%, Cicarelli), colloidal silica (Ludox HS-30, Sigma-Aldrich), sodium aluminate (99%, Sigma-Aldrich) and double deionized water. All the syntheses were performed according to the following gel composition: $9.5Na_2O$: $1.0Al_2O_3$: $14.0SiO_2$: $288H_2O$. The synthesis gel molar composition was adjusted in agreement with the bibliography [13,14,18]. The precursor gel was prepared mixing the required amounts of sodium hydroxide and deionized water into a polypropylene bottle. After complete dissolution, sodium aluminate and colloidal silica were added, and the mixture was homogenized under vigorous agitation.

Subsequently, the synthesis procedure was performed in two stages (Scheme 1). In the first stage, the precursor gel was sonicated in the water bath (47 KHz, 130 W) for 1 hour (Na-Y1). In addition, for comparative purposes the same gel synthesis was kept under mechanical stirring at the same time (Na-Y0). Then precursor gels with different pretreatment were aged for 20 h at 30 °C.

Finally, the samples Na-Y0 and Na-Y1 were hydrothermally treated at 60 °C for 48 hours under static condition (Na-Y0-60 and Na-Y1-60) taking into consideration the industry requirement of low-temperature hydrothermal techniques [13]. Additionally, the hydrothermal treatment was carried out at

100 °C for 24 hours (Na-Y0-100 and Na-Y1-100) in order to study the effect of different crystallization temperature and time. The final products were recovered by filtration, washed with deionized water until pH = 8-9 and dried at 100 °C for 24 h.

Scheme 1.

2.2. Characterization

The crystalline structures of synthesized samples were determined by X-ray diffraction using Philips PW1710 diffractometer with Cu Kα radiation (λ=1.5406Å) operated at 45 kV and 30 mA. The diffraction patterns were collected in the 2θ range of 2-40° at 0.25°/min with a step size of 0.02°. The primary crystal size was estimated from Scherrer equation at the peaks 2θ of 6.2° (111), 15.5° (331), 23.4° (533) and 26.8° (642). The degree of crystallinity of all samples was determined roughly by comparing the peaks area at Bragg angle 2θ between 6 and 35°. The sample prepared in this study with the highest intensity was taken as reference assigning 100% of crystallinity [16].

The morphology and particles size were analyzed by scanning electron microscopy (SEM) on an EVO 40 XVP (10 kV) instrument. The structure and crystal average were evaluated by Transmission Electron Microscopy (TEM) using JEOL 100 CX II (acceleration voltage of 200 keV).

The textural characterization of the solids was obtained from the N_2 adsorption- desorption isotherm at 77 K on ASAP 2000 Micromeritics instrument. Prior to measurement, the samples were evacuated 12 hours at 150 °C. The specific superficial area (S_{BET}) was estimated by the Brunauer, Emmet

and Teller (BET) method using the considerations proposed by Rouquerol et al. [28]. The external surface area (S_{Ext}) and micropore volume (V_{micro}) was determined by the α-plot method [29]. Total pore volume was estimated from desorption isotherm branch at $P/P_0=0.98$ assuming complete pore saturation. The micropore and mesopore size distribution were calculated by Non-Local Density Functional Theory (NLDFT) and Berrett Joyner Halenda (BJH) method respectably.

The framework Si/Al ratio was determinate by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using high-resolution Shimadzu 9000 multitype instrument.

3. RESULTS AND DISCUSSION

The XRD patterns corresponding to the samples obtained with different treatment are shown in Fig. 1. XRD pattern indicated that all samples correspond to pure well crystalized FAU zeolite-type structure. Crystallinity degree results are shown in Table 1. Sonication aging results in high crystalline samples for the different hydrothermal treatment. As expected, the sample Na-Y1-100 synthesized at higher hydrothermal temperature and using sonication shows better crystallinity.

The primary crystal size estimated from the Scherrer equation corresponds to very small crystals smaller than 45 nm (Table 1). It can be seen that the application of ultrasound at the aging stage decreases the crystallite size ~15 % for the two hydrothermal temperatures used in this study. Moreover, as can be seen in Table 1, the ICP-AES analysis indicated that the samples SiO_2/Al_2O_3 molar ratios are between 2.5-3.0 which correspond to FAU-Y zeolite

[30]. The SiO_2/Al_2O_3 molar ratio in framework increased when the sonication pretreatment was applied. This could be attributed to the fact that sonication energy increases the concentration of soluble silicate species, thus enabling their incorporation into tetrahedrally coordinated framework [31].

The Scanning Electron Microscopy (SEM) micrographs of the synthetized zeolites are presented in Fig. 2. The zeolite particles obtained in this work exhibits closely nanocrystal aggregates with uniform particle size distribution. The samples Na-Y0-60 and Na-Y0-100 synthesized using mechanical agitation at the aging stage have a mean particle size of ~252 and 345 nm (Table 1) in the range between 110-370 and 220-470 nm, respectively. However, the zeolites obtained via ultrasound pretreatment show slight particle size reduction. As shown in the particle size distribution (Fig. 2), the samples Na-Y1-60 and Na-Y1-100 have a mean particle size of ~224 and 296 nm, respectively. As can be seen, the morphology and particle size using different hydrothermal conditions is not substantially influenced by ultrasound application in the aging stage.

Furthermore, the structure of the synthesized material was elucidated by transmission electron microscopy (TEM). The representative TEM images at low magnification (Figure 3.a) reveals similar particles size distribution to those obtained by SEM (Table 1). TEM micrographic at high magnification indicates the presence of polycrystalline FAU particles composed of many closely packed nanocrystals with regular shape and size between 30-45 nm in good agreement with XRD data.

Also, the success in zeolite NaY synthesis in terms of crystallinity and particle size (in nanoscale order <350 nm) in the organic free system and low

costs procedures could be attributed to the proposed synthesis strategies that include the precursor gel composition design and synthesis conditions selected.

The synthesis gel molar composition is a critical factor in zeolites synthesis methodologies. It was found that a high Na_2O content in the reaction mixture induces a crystalline size decrease because of nucleation increase [8,16] and a high Si/Al ratio can retain relatively high crystallinity during the hydrothermal treatment [32]. Kim et al. [18] used an experimental design to prove the Na_2O/Al_2O_3 molar ratio ~10 significantly reduces crystal agglomeration. Additionally, previous work [17,18] suggest that water content plays an important role in crystal size control. The results obtained shows that the particle size considerably increases for H_2O/SiO_2 molar ratios above to 22. In the present study, in order to achieve pure FAU crystals in nanoscale size the molar ratios: Na_2O/Al_2O_3=9.5, SiO_2/Al_2O_3=14 and H_2O/SiO_2=20.6 were appropriately adjusted on the basis of the bibliographic reports [16-18].

On the other hand, the aging step prior to crystallization strongly affects the crystal size by the increase in the number nuclei that promotes the pure phase FAU formation [9,33]. An increase in aging temperature (>30 °C) and time (>24 h) results in substantially larger zeolite particle sizes [13,14,18]. Previous reports [13,18] indicated that the best temperature range is between 25 to 30 °C. At a given temperature and 20 hours of aging treatment the particle size was decreased to its minimum, whereas at longer time the particle size begins to increase [14].

Furthermore, the present study shows that ultrasonic-assited aging enables a reduction in the crystal size. The physical phenomenon involved in sonication is acoustic cavitation that generates high energy shock waves, thus

increases the nucleation rates. Also, the fast bubble collapses produce a high rate of temperature decrease which prevents the organization and agglomeration of the particles, leading to small size crystal formation [23,25,30].

Finally, the main factors involved in crystallization process, which affect the crystal size, are the synthesis time and temperature. Low crystallization temperature (60-100°C) is often applied because temperature leads to higher crystal growth rates in comparison to nucleation rates. Nevertheless, lower temperatures (<40°C) usually result in poor crystallinity, low efficiency, and longer crystallization time [21]. The crystallization time strongly depends on temperature: low temperatures demand long crystallization time while at high temperatures the required time is less [13,16]. Accordingly, the crystallization process at 60 °C during 48 hours results in pure FAU phase formation with a crystal size of ~33 nm. Moreover, the crystallization process carried out at 100 °C for 24 hours allowed a well crystallized FAU phase with a larger size (~44 nm) than the one obtained at lower temperature and longer crystallization time. The same trend was observed in the synthesis procedure made using ultrasound pretreatment and different hydrothermal condition.

Figure 1.

Table 1.

Figure 2.

Figure 3.

Figure 4 presents FAU zeolites N_2 physisorption isotherm. The N_2 adsorption - desorption isotherms for the samples obtained in this study present a Type I profile [34]. The porous materials synthetized show an initial adsorption step at very low relative pressure (P/P_0=0.02), indicating the complete filling of the micropores. The sample synthesized using sonication shows higher N_2 adsorption capacity than the nanozeolite obtained by conventional hydrothermal method because of its higher crystallinity. This same behavior is appreciated for both thermal treatments.

Moreover, the small hysteresis loops in the N_2 adsorption - desorption isotherm curve for the porous monocrystalline zeolites at high relative pressure suggest some mesoporous presence. The materials mesoporosity results from filling of intercrystalline voids shaped in the nanocrystals packing due to their spherical morphology. The hysteresis loop at relative pressure between 0.45-0.85 is associated with slit-shaped pores, while the hysteresis loop at high relative pressure (P/P_0=0.85-1.00) corresponds to more spherical voids [17,35,36].

Pore size distributions obtained applying the DFT and BJH model to nitrogen adsorption data are shown in Figure 5. All the synthetized nanozeolites present a well-defined porous structure which consists of micropores with an average diameter of 1.1, 1,27 and 1.45 nm resulting from the intrinsic FAU zeolite structure and crystalline defects. The mesopores present a pore diameter about 8.5 nm arising from the aggregation of the nanocrystal. These results are highly attractive since the combination of micro and mesopores is important for many industrial applications. A hierarchical pore system facilitates mass transport while maintaining the zeolite shape selectivity [37]. Abildstrøm et

al. [38] indicated that the introduction of an even moderate degree of mesoporosity during the synthesis could improve the ability for the ion exchange of zeolite Y and thus lead to an improved and more stable ion exchange process at industrial scale.

The zeolites textural properties measured from nitrogen isotherms (at 77 K) are listed in Table 2. The zeolites obtained in this work present a BET surface area higher than the similar nanocrystal (25-50 nm) reported elsewhere [5,17]. Also, the nanozeolites synthetized using an aging pretreatment with ultrasound present slightly larger external surface area and pore volume than those obtained employing mechanical agitation during the aging pretreatment. Additionally, the hydrothermal temperature slightly affects the external surface area and pore volume. These results are in correspondence with higher crystallinity and smaller crystal size. Previously reports [35,39] showed that an increase in the external surface area is consistent with a reduction in particle size due to the number of crystals per crystallites present in the material. Asakari et al. [23] demonstrated that the samples synthesized by the sonication presented high BET surface, attributed to the spherical SAPO-34 nanocrystals with a uniform morphology which are dispersive among each other; thus, leading more cell crystals and more pore mouths exposed and resulting in an external and BET surface area increase.

As demonstrated in previous works [40,41] the crystal dimensions can be estimated using the external surface area (S_{ext}) assuming cubic crystals geometry according to the relationship below:

$$D_{ext}=4061/S_{ext}$$

The estimated results (Table 2.) correspond to the smallest crystal size and are in accordance with crystallite sizes determined by Scherrer equation. The crystal size decreases with the application of sonication in the aging step.

Figure 4.

Figure 5.

Table 2.

4. CONCLUSION

Zeolite Na-Y nanoparticles were synthesized via an alternative and green process without organic template and low temperature. The synthesis method was a very simple, fast, efficient and environmentally friendly route to obtain nanocrystalline zeolite. It was performed in two stages that include aging step applying ultrasound pretreatment and a hydrothermal treatment.

The sonochemical pretreatment influences the Na-Y zeolite properties. Average crystal size, particle size distribution decreased and the textural properties change slightly. This fact is attributed to the contribution of the sonochemical process energy that induces the formation of a greater number of nuclei favoring the crystallization stage. The material obtained using ultrasound aging stage and different hydrothermal conditions corresponds to pure faujasite zeolite type with small crystal size in nanoscale order between 28 and 38 nm. Also, the hierarchical nanozeolite exhibits high superficial area BET (850 and 950 m^2g^{-1}) and combines micro- and mesopores. The results are highly

attractive for many industrial applications due to the simplicity of the synthesis procedure and remarkable nanozeolite properties.

5. ACKNOWLEDGEMENTS

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Table 1. Nanocrystal and particles sizes of synthetized porous Na-Y zeolite.

Samples	Crystal sized (nm)[a]	Crystallinity (%)	Particle sized from SEM (nm)[b]	Particle sized from TEM (nm)[c]	Si/Al molar ratio[d]
Na-Y0-60	33	73.5	252	246	2.5
Na-Y1-60	28	76.1	224	205	2.9
Na-Y0-100	45	88.0	345	350	2.6
Na-Y1-100	38	100.0	296	280	3.0

[a] Calculated by XRD using Scherrer equation

[b,c] Calculated by SEM and TEM image at low magnification respectively

[d] Obtained from ICP-AES analysis

Table 2. N_2 adsorption-desorption results of porous Na-Y zeolite synthetized

with different aging pretreatment and hydrothermally condition

Samples	S_{BET} $(m^2/g)^a$	S_{Ext} $(m^2/g)^b$	V_{Micro} $(cm^3/g)^b$	V_{Meso} $(cm^3/g)^c$	V_{Total} $(cm^3/g)^d$	V_{Micro} (%)	D_{Ext} $(nm)^e$
Na-Y0-60	840	124	0.27	0.12	0.39	65.8	32.7
Na-Y1-60	880	134	0.27	0.14	0.41	69.2	30.3
Na-Y0-100	850	112	0.28	0.10	0.38	73.7	36.3
Na-Y1-100	950	121	0.31	0.11	0.42	73.8	33.6

[a] BET surface area
[b] α-Plot method
[c] $V_{Meso} = V_{Total} - V_{Micro}$
[d] Evaluated by the single-point desorption at $P/P0 = 0.98$
[e] Obtained using the equation $D_{Ext} = 4061/S_{Ext}$ [41,42]

Highlights

- Alternative green methodology of nanocrystalline faujasite zeolite synthesis has been proposed.

- Ultrasonic irradiation was applied on aging stage.

- Sonochemical procedure has influences on Na-Y zeolite final properties.

- Hierarchical faujasite nanozeolite exhibits elevated surface area and combines micro- and mesopores.

| **Precursor gel synthesis** | **Stage 1. Aging pretreatment** | **Stage 2. Hydrothermal treatment** |

Gel composition:

$9.5Na_2O:1.0Al_2O_3:14.0SiO_2:288H_2O$

Mechanical agitation 1 h — 20 h–30°C

Sonication (47 KHz) 1 h — 20 h–30°C

48h - 60°C

Na-Y0-60 / Na-Y1-60

24h - 100°C

Na-Y0-100 / Na-Y1-100
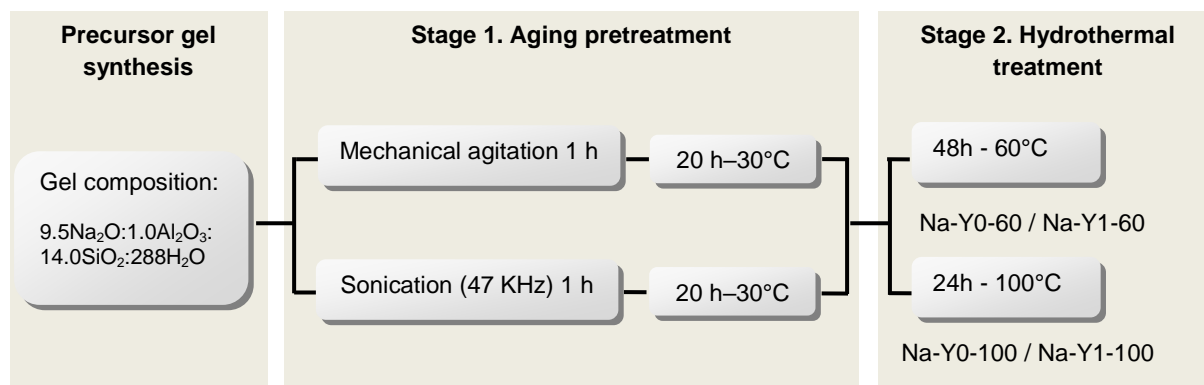
Scheme 1. Stages of nanoparticles Na-Y zeolite synthesis process.
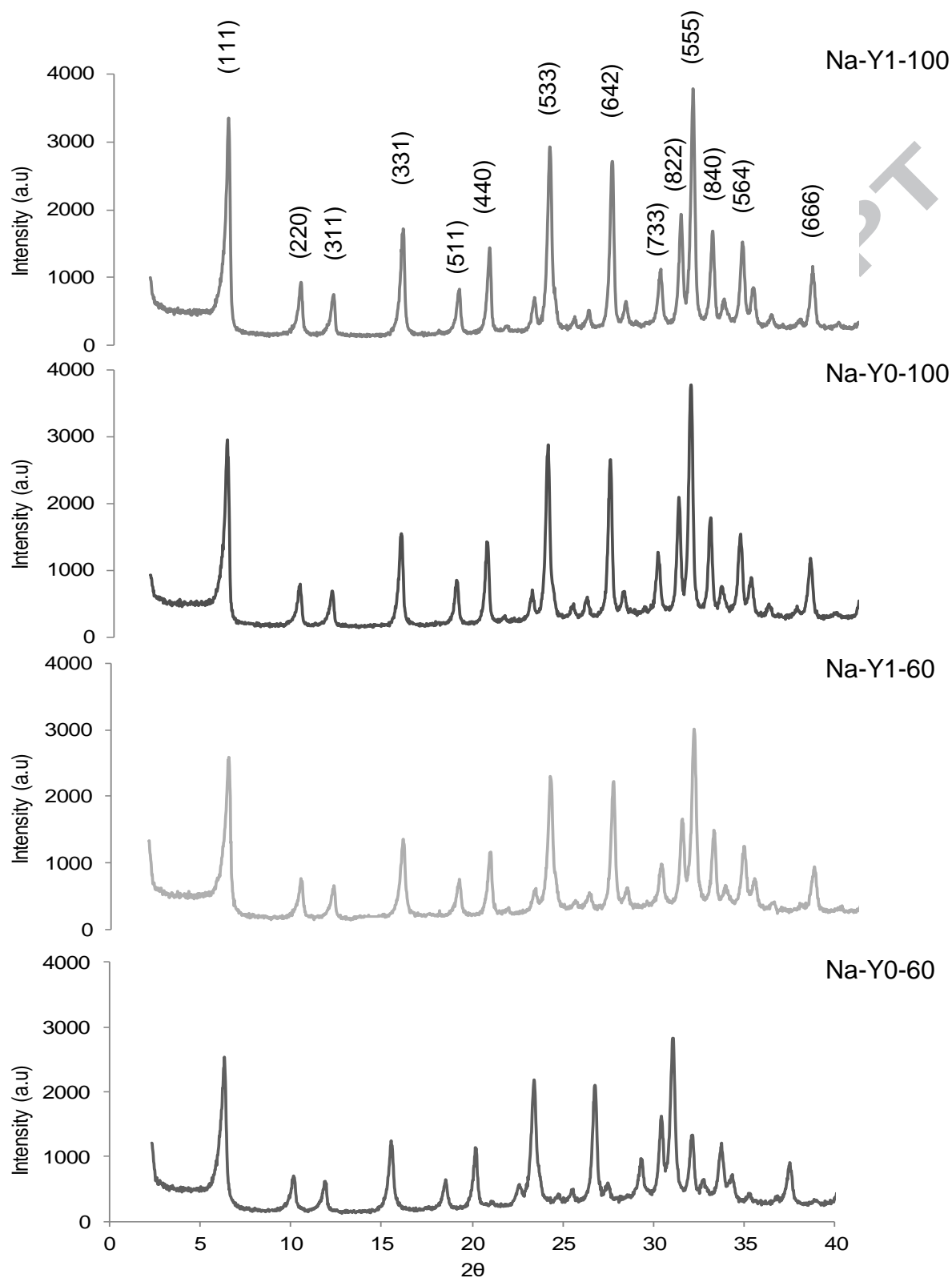
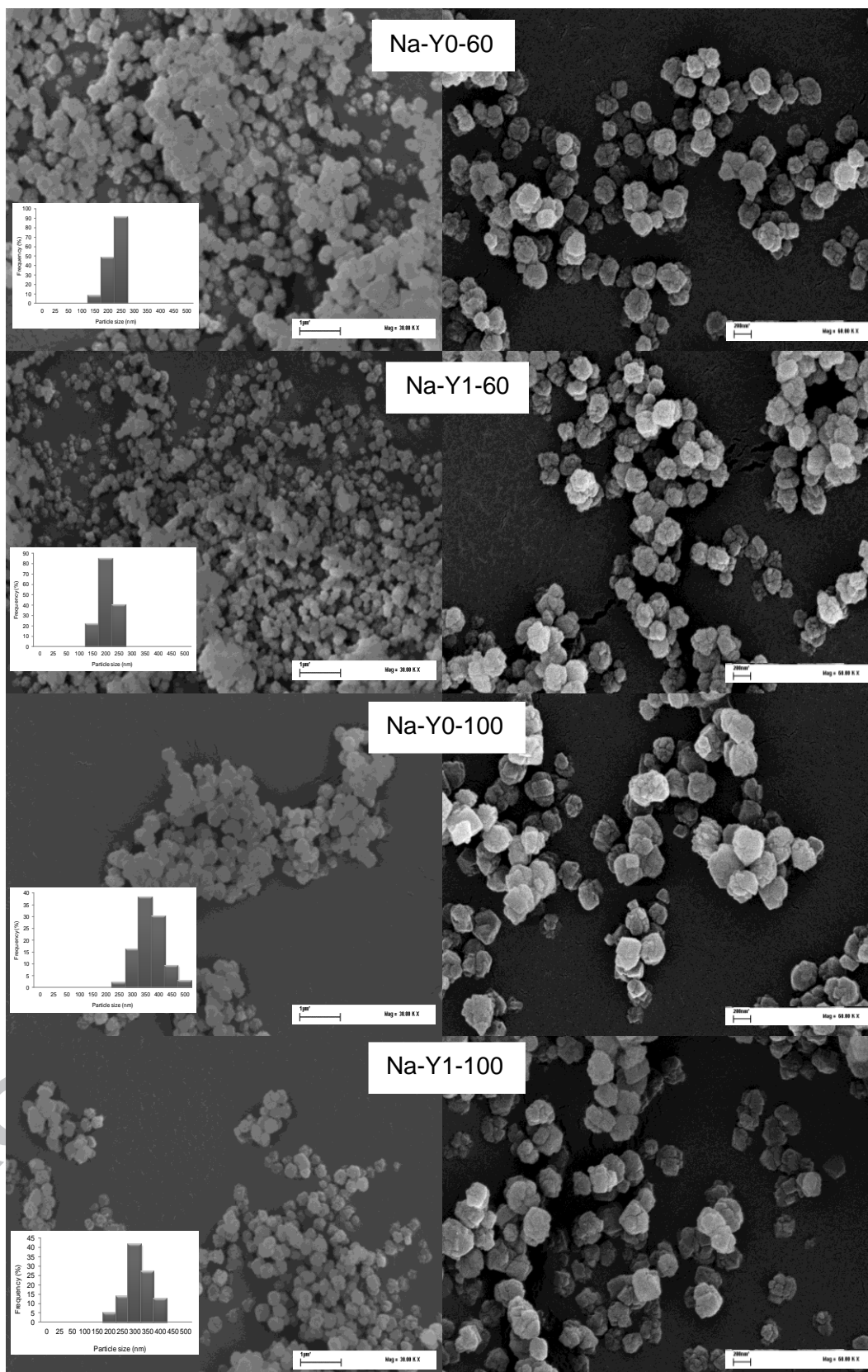**Figure 1.** XRD pattern of samples synthesized with different aging pretreatment and hydrothermally condition.

Figure 2. TEM image of samples synthesized with different aging pretreatment and hydrothermally condition.
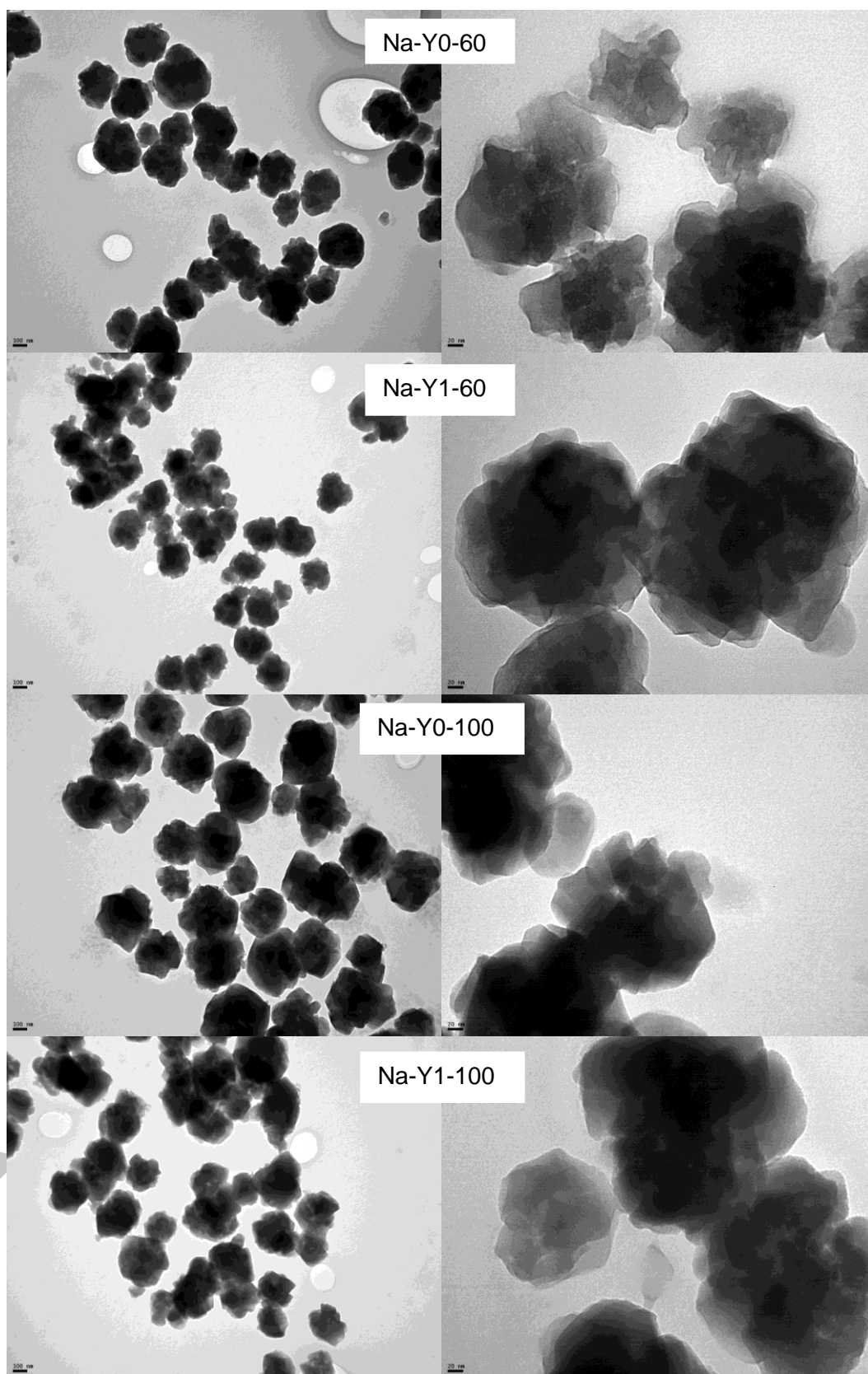
Figure 3. TEM image at low (a) and high (a) magnification of samples synthesized with different aging pretreatment and hydrothermally condition.
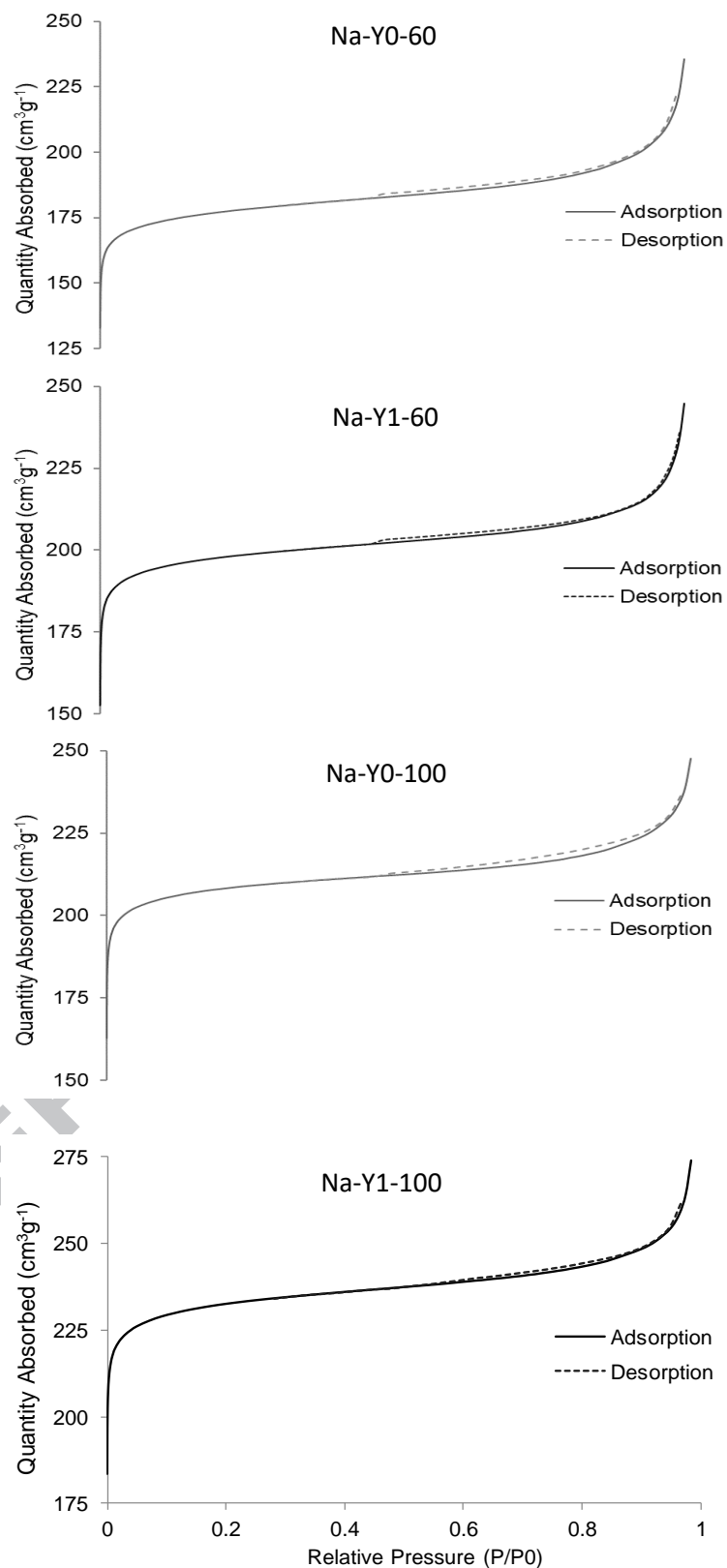
Figure 4. N_2 adsorption-desorption isotherms synthetized nanozeolites with different aging pretreatment and hydrothermally condition.
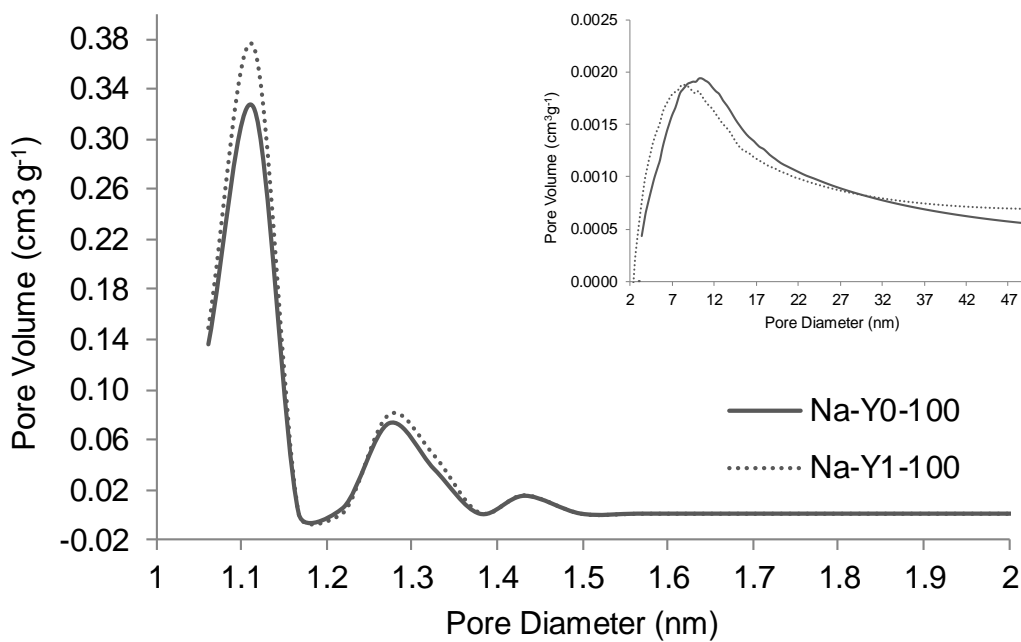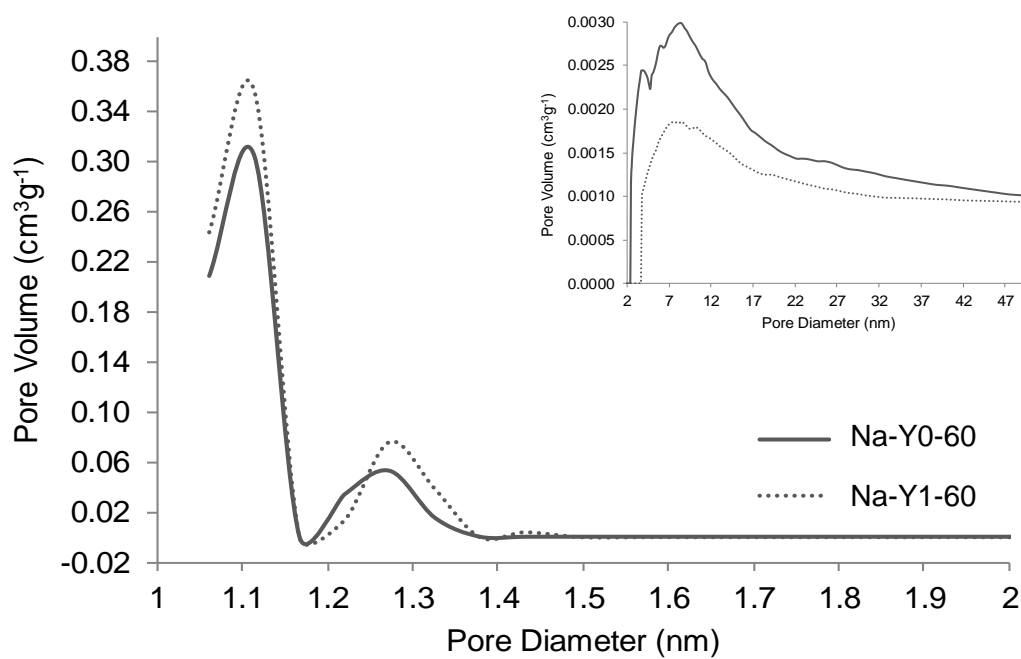
Figure 5. Pore size distribution for samples synthesized with different aging

pretreatment and hydrothermally condition.