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Effects of Synthetic Conditions on Structure of Nanocrystal Zeolite Y From Vietnamese Kaolin

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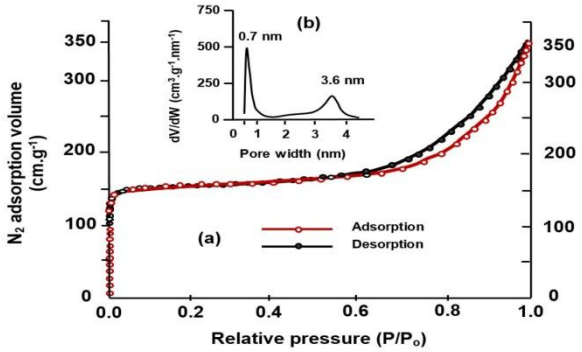
ABSTRACT

In this paper, synthetic parameters affecting the crystal size, bulk density and structure of nanocrystals zeolite NaY from Vietnamese kaolin at ambient pressure such as feedstock pretreatment, the Na_2O/Al_2O_3, SiO_2/Al_2O_3, H_2O/Al_2O_3, $EDTA/Al_2O_3$ and $NaCl/Al_2O_3$ ratios were investigated. Characterizations including XRD, TEM, FT-IR, TPD-NH_3 showed that the water molar ratio strongly affected to the crystal size of the zeolite Y. Decrease of water content in the gel sharply reduced the crystal size of zeolite Y. The Na_2O/Al_2O_3 also had strong effect on the crystal size of nano zeolite Y. The too low value of the Na_2O/Al_2O_3 molar ratio was not a favourable environment for the dissolution of precursors and the creation of SBU in the crystallization. In contrast when the ratio of Na_2O/Al_2O_3 was too high, the generated nanosized crystals were partially dissolved. The optimum Na_2O/Al_2O_3 ratio was 3.5 to obtain the smallest crystal size of 20nm. EDTA and NaCl could also be used to control crystal size. Results from ^{27}Al-NMR and bulk density confirmed that synthetic parameters had strong effects on the crystal size and bulk density. However among other synthetic parameters, just SiO_2/Al_2O_3, Na_2O/Al_2O_3 and $NaCl/Al_2O_3$ molar ratios had strong effect on the nature of aluminum sites in the as-synthesized materials. Optimum synthetic parameters would generate most tetrahedral aluminium sites which were expected structure of good catalysts.

Graphical Abstract:



Keywords: Zeolite, Nano crystals, Crystallinity, Crystal size, Kaolin.

INTRODUCTION

Kaolin has been used for the synthesis of zeolite as aluminum precursor [1-2]. Prior to the synthesis, kaolin must be pretreated at 600–700 ^{o}C to be converted to metakaolin. Zeolite directly synthesized from metakaolin normally has crystal size range from over 100 nm similar to the zeolite synthesized from pure chemicals. However, using kaolin for the synthesis of zeolite nanocrystals was still limited due to the impurities of this raw material. Recently few papers were published about the production of zeolite nanocrystals from kaolin but with very different methods [3-6]. K. Shams et al reported that zeolite A nanocrystals with average crystal size of about 260 nm were prepared from the sodium aluminate (from metakaolin) in 8hrs at 75 ^{o}C by nanoemulsion-ultrasonic technique [3]. M. Khatamian reported that zeolite ZSM-5 nanocrytals were produced from the crystallization of metakaolin, tetrapropylammonium hydroxide (TPAOH), boric acid, silicic acid, sodium hydroxide and distilled water in 72–168 h at 120–180 ^{o}C [4]. Nanocrystals obtained at 180 ^{o}C after 168 h have avarage size of 20–42 nm. X.J. Wang et al reported that the of nano-zeolite NaY from metakaolin by ionothermal method with microwave assisted was very complicated. Metakaolin was used as aluminum precursor with seed solution (from sodium silicate and sodium aluminate solutions) [5]. Zeolite NaY nanocrystals were formed at 90^{o}C during 12hrs with crystal size of about 150–250 nm and crystallinity of 69,16 %. In [6] zeolite NaX nanocrystals were directly prepared at ambien pressure during 12hrs at 80 ^{o}C by hydrothermal synthesis. At optimized synthesis conditions, nano-zeolite NaX has surface area of 573 m^2 g^{-1} with external surface area of 92 m^2 g^{-1}, pore size distribution at 0.81 and 10.8 nm, average crystal size of 25 nm and thermal stability up to 789 ^{o}C. It can be seen that the directly synthesis of zeolite NaY nanocrystals by hydrothermal synthesis from Kaolin at ambien pressure hasn't been reported. This paper reported effects of synthetic conditions on the crystal size and the structure of nano NaY from Vietnamese metakaolin at ambient pressure. Optimum synthetic parametters were discussed and reported herewith.

MATERIALS AND METHODS

Synthesis of nanocrystals zeolite NaY:

Table 1. Nanocrystal zeolite Y with different synthetic conditions and gel molar ratio

No.	Samples	HCl (M)	H_2O/Al_2O_3	SiO_2/Al_2O_3	Na_2O/Al_2O_3	$NaCl/Al_2O_3$	$EDTA/Al_2O_3$
1	Y-0M	0					
2	Y-2M	2					
3	Y-4M	4	70	7	3.5	3	1.2
4	Y-6M	6					
5	Y-8M	8					
6	Y-70H		70				
7	Y-90H		90				
8	Y-110H	4	110	7	3.5	3	1.2
9	Y-130H		130				
10	Y-150H		150				
11	Y-5S			5			

12	Y-6S			6			
13	Y-7S	4	70	7	3.5	3	1.2
14	Y-8S			8			
15	Y-9S			9			
16	Y-2.5N				2.5		
17	Y-3.0N				3.0		
18	Y-3.5N	4	70	7	3.5	3	1.2
19	Y-4.0N				4.0		
20	Y-4.5N				4.5		
21	Y-0NaCl					0	
22	Y-1NaCl					1	
23	Y-2NaCl	4	70	7	3.5	2	1.2
24	Y-3NaCl					3	
25	Y-4NaCl					4	
26	Y-5NaCl					5	
27	Y-E0.0						0.0
28	Y-E0.3						0.3
29	Y-E0.6						0.6
30	Y-E0.9	4	70	7	3.5	3	0.9
31	Y-E1.2						1.2
32	Y-E1.5						1.5
33	Y-E1.8						1.8

Five sample of kaolin with same weight were treated with hydrochloric acid solutions with concentrations 0,2M, 4M, 6M and 8M with ratio of solid/liquid = 2/3 (g /ml) in 6 h at 90 ^{o}C. After the activation, samples were filtered through ion Cl^{-} washed and dried for 2 hrs at 110 ^{o}C. Obtained kaolin samples were then treated with acid, named as Kao-nM respectively (where n = 0–8). As-treated kaolin samples were continuously heated for 3 h at 650 ^{o}C in atmospheric pressure to create metakaolin (named as Meta-nM).
Metakaolin was then mixed with liquid glass, sodium hydroxide, EDTA, sodium chloride and distilled water. The molar composition of initial gel was aNa$_2$O · Al$_2$O$_3$ · bSiO$_2$ · cH$_2$O · dEDTA · eNaCl (whereas a = 2.5–4.5; b = 5–9; c = 70–150; d = 0.0–1.8; e = 0–5). The obtained solutions were aged at room temperature in 144 hrs and hydrothermal crystallized at 80 ^{o}C in 12 hrs in autoclave at autogenous pressure. Molar composition, crystallizing condition and sample codes are presented in table 1.Obtained nanozeolites were repeatedly washed with distilled water until pH of supernatant was 8. Nanoparticles were dried at 110 ^{o}C and calcined at 550 ^{o}C.

Characterization of as-synthesized zeolites: Chemical compositions of kaolin and as-synthesized zeolite NaY samples were studied [7]. SiO_2 content was determined by the melting method. The elements in the form of Al_2O_3, Fe_2O_3, FeO, CaO, MgO were determined by EDTA titration. The weight loss (MKN) was studied as samples calcined at 950 ^oC. Content of Na_2O, K_2O and TiO_2 was determined by atomic absorption method (AAS).
It has been widely known that in kaolin and samples synthesized from kaolin, the cation exchangeable was mainly Na^+, K^+, Ca^{2+} and Mg^{2+} [8]. Total exchange capacity measured per 100 g sample (meq/100g) and was determined by the ion exchange method [7]. The principle was using $BaCl_2$ solution 1N to exchange the ions in the study sample. Then the ion-exchanged samples reacted with H_2SO_4 solution 0.05N H^+ ion. The titration of the excess H_2SO_4 was the carried out with 0.05N NaOH. Phenolphthalein indicator will calculate the total exchange capacity of the sample.

X-ray Diffraction (XRD). A Siemens D5005 X-ray diffractometer with Cu Kα target and nickel filter was used to collect XRD powder patterns for the samples. XRD patterns were collected between 2θ angles of 5 and 45° for the parent zeolite to confirm the crystal phase. Narrow-range patterns were collected from 2θ = 23–24 with a 0.01 2θ step size, 10 s/step. The full-width at half maximum (FWHM) of the peak from the slow scan of each sample was obtained by simulation and was used to estimate the crystal size of each nano-zeolite NaY sample from Scherrer's equation (with K = 1.0):

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

In which, τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; K is a dimensionless shape factor, with a value close to unity; λ is the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as Δ(2θ); θ is the Bragg angle [4].

The crystallinity of the samples in XRD patterns were calculated as equation:

%Crystallinity = (total area of crystalline peaks) / (total area of all peaks)

Transmission electron microscopy (TEM) and Scanning electron micro spectroscopy (SEM): TEM and images of the nano-zeolite crystals were acquired using a JEM-1010 electron microscope.

Fourier transform infrared (FT-IR): FT-IR spectra in the nano-zeolite framework vibration region were obtained with a Nicolet impact FT/IR-410 spectrometer using the KBr pellet technique. Each spectrum was acquired in a wavenumber range between 400 and 1300 cm^{-1} at a 2 cm^{-1} resolution.

Nitrogen adsorption–desorption measurements were carried out at –196 ^oC on a Micromeritics ASAP 2010 instrument to determine the Brunauer–Emmett–Teller (BET) surface area and to estimate the mesopore size distribution using the Barrett–Joyner–Halenda (BJH) calculation procedure [9]. Before each measurement, samples were vacuated overnight at 100 ^oC and < 1 µm Hg. Higher temperatures were not used so that occluded template in the zeolite structure would not decompose or volatilize. The total pore volume, V_{total}, was taken from the desorption branch of the isotherm at P/Po = 0.995 assuming complete pore saturation. The volume of the micropores, V_{micro}, was determined by the *t*-plot method. The volume of the mesopores, V_{meso}, was estimated from the equation: $V_{meso} = V_{total} – V_{micro}$.

NMR data: The ^{27}Al MAS NMR experiments were run on a Varian Infinity plus AS400 spectrometer at 104.26 MHz, with a pulse width of 0.5 µs, radio frequency field strength of 50 V/m, a pulse delay of 0.5 s, a spinning rate of 4 kHz and 85,000 scans.

RESULTS AND DISCUSSION

Effects of feedstock pretreatment on the nanocrystals zeolite NaY: Table 2 showed the chemical compositions of 5 samples of un-treated kaolin and samples treated with HCl of different concentration together with 5 as-synthesized samples respectively.

Table 2. Chemical compositions of un-treated kaolin, treated with HCl and as-synthesized nano crystal zeolite Y, %

No.	Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	K_2O	Na_2O	LOI	%, wt	Mol SiO_2: Al_2O_3	CEC, meq/100g
1	Kao-0M	47.23	35.52	1.25	0.08	0.07	0.36	0.22	2.43	0.24	12.53	99.93	2.26	12
2	Kao-2M	51.38	32.13	0.90	0.08	0.06	0.30	0.24	2.65	0.22	12.02	99.98	2.72	13
3	Kao-4M	53.42	30.56	0.56	0.07	0.06	0.28	0.28	2.78	0.20	11.54	99.75	2.97	13
4	Kao-6M	55.24	28.81	0.34	0.07	0.06	0.22	0.34	2.99	0.18	11.23	99.48	3.26	14
5	Kao-8M	59.35	25.48	0.22	0.07	0.06	0.20	0.43	3.12	0.15	10.82	99.90	3.95	14
6	Y-0M	50.34	19.88	1.02	0.07	0.06	0.36	0.20	2.21	8.39	17.23	99.76	4.30	210
7	Y-2M	47.25	20.34	0.62	0.06	0.06	0.32	0.20	2.20	9.52	19.28	99.85	3.94	235
8	Y-4M	46.24	20.26	0.40	0.05	0.04	0.18	0.23	2.13	9.94	20.47	99.94	3.88	261
9	Y-6M	48.58	20.42	0.35	0.06	0.07	0.18	0.23	2.73	8.60	18.57	99.79	4.04	216
10	Y-8M	51.04	18.90	0.20	0.06	0.06	0.22	0.20	2.67	8.45	18.02	99.82	4.59	205

It was shown (table 2) that un-treated kaolin (Kao-0M) has the lowest SiO_2, K_2O and MgO content but highest content of Al_2O_3, Fe_2O_3, CaO, Na_2O and loss on ignition (LOI). When HCl concentration for kaolin treatment increased from 2M to 8M, the chemical composition are either increased or decreased linearly. This showed that the higher HCl concentrations treated, the higher solubility of Al_2O_3, Fe_2O_3, CaO, Na_2O and LOI. LOI included organic contaminants and physical forms of water (surface-absorbed water, water absorbed between layers of the network structure of kaolin). As a result the SiO_2/Al_2O_3 molar ratio increased from 2.26 to 3.95. Table 2 also showed that the raw materials had much lower Na_2O and LOI than the as-synthesized samples respectively. This proved that the two-dimensional layer structure of kaolin was converted successfully into 3-dimensional structure of the zeolite. The increase in the concentration of Na_2O and LOI in synthesized samples was due to Na^+ and OH^- has gone into the structure of the zeolite. Kaolin and treated kaolin had very small amount of CEC (cation-exchange capacity) (from 12 to 14 meq $100g^{-1}$) because they had two-dimensional layered structure with very low porosity. All 5 synthesized samples had very large CEC (from 205 to 261 meq $100g^{-1}$), showing the structure of kaolin layers were converted into three-dimensional structures with higher porosity. In the 5 samples, the sample zeolite Y-4M as-synthesized from kaolin treated with HCl 4M (Kao 4M) had largest cation exchange capacity, this could be explained that the sample contained largest amount of AlO_4^- tetrahedral.

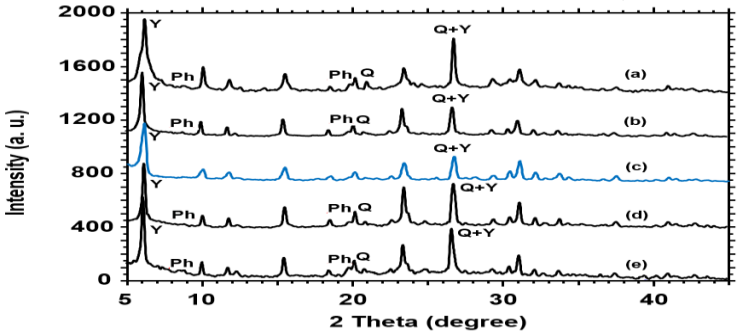


Figure 1. Stacked XRD of samples Y-0M (a), Y-2M (b), Y-4M (c), Y-6M (d) and Y-8M (e). Y: zeolite NaY, Ph: Phlogopite, Q: α-quartz; Q+Y stand for two peaks of two phases of zeolite and α-quartz at the same 2-Theta positions.

XRD and FWHM data of as-synthesized samples (figure 1) showed the differences in the crystallinity and crystal sizes. The smallest crystal size of 20nm was found in the sample prepared from kaolin treated with HCl 4M which has the lowest SiO_2/Al_2O_3 ratio = 3.88. Figure 1 also showed the appearance of two other phases of Ph-phlogopite at 2θ value = 8.9, 19.8 and Q–quartz at 2θ = 20.9 and 26.7 in all sample. But in sample Y-4M these XRD peaks were with weakest intensity showing the highest crystallinity of zeolite Y phase.

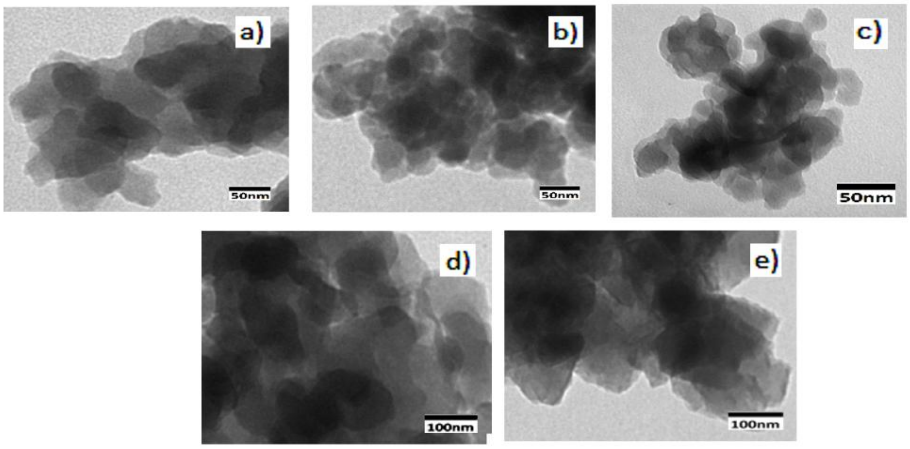


Figure 2. TEM images of Y-0M (a), Y-2M (b), Y-4M (c), Y-6M (d) and Y-8M (e).

TEM image (figure 2) showed fine crystals with particles size of 20 nm in sample Y-4M (this is similar to the result in table 3 determined by XRD according to equation Scherrer's [10]). These two methods give similar results show samples containing zeolite NaY nanocrystals with uniform sizes. It is obviously that different pretreatment of feedstock led to differences in SiO_2/Al_2O_3 molar ratio in as-synthesized samples as well as the nanocrystal sizes. In this study raw kaolin treated with HCl 4M and calcined at 650 ^oC was the best precursor for the synthesis of zeolite NaY nanocrystals.

Table 3. Effects of feedstock pretreatment on the as-synthesized zeolite NaY nanocrystals.

No.	Samples	XRD	
		Crystallinities, %	Crystal sizes, nm
1	Y-0M	82	40
2	Y-2M	92	32
3	Y-4M	95	20
4	Y-6M	85	85
5	Y-8M	80	120

Effect of water molar ratio in the gel on the nanocrystals zeolite NaY:

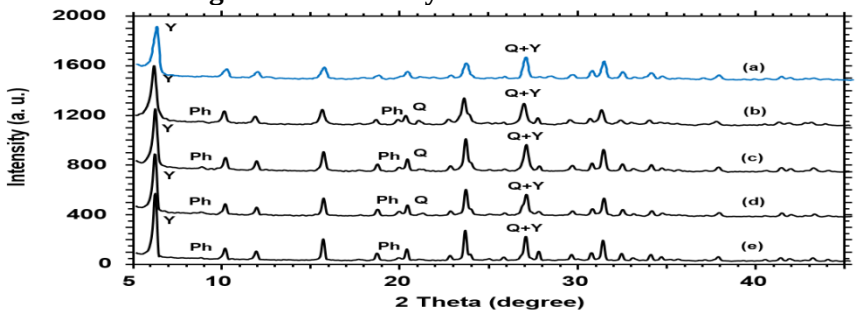


Figure 3. XRD patterns of samples : Y-70H (a), Y-90H (b), Y-110H (c), Y-130H (d) and Y-150H (e). Y: zeolite NaY, Ph: Phlogopite, Q: α-quartz; Q+Y stand for two peaks of two phases of zeolite and α-quartz at the same 2-Theta positions.

Effect of water molar ratio in the gel on the nanocrystals zeolite Y was investigated through XRD and TEM methods, shown in figure 3,4 and table 4. Results showed that the increasing water molar ratio in the gel , the decreasing the crystallinity of the as-synthesized zeolites and the bigger size the zeolite Y crystal. The crystal size of the zeolites increased sharply from 20 to 120 nm with molar ratio of H_2O/Al_2O_3 went from 70 up to 150. This was because when increasing the water content in the gel composition, the concentration of the AlO_4^- and SiO_4 tetraherons in the gel decreased. As a result, the crystalization slowed down, and the small crystals could be combined to become larger crystals. Other experiments with molar ratio of H_2O/Al_2O_3 less than 70 were also studied, but the gels were too condensed to be stirred and crystallized.

Table 4. Effect of water content on crystal sizes of zeolite NaY nanocrystals

No.	Samples	XRD		CEC, meq/ 100g
		Crystallinities, %	Crystal sizes, nm	
1	Y-70H	95	20	261
2	Y-90H	92	80	232
3	Y-110H	92	125	227
4	Y-130H	92	136	220
5	Y-150H	90	200	218

TEM images showed clearly the fine crystal morphologies. The crystal sizes from TEM were compatible with that of XRD method. This study showed that to obtain zeolite with nanocrystal size under 100 nm, the H_2O/Al_2O_3 ratio should not be over 90. Table 4 also indicated that the CECs decreased when the water content in the gel composition decreased. It was because the crystal size increased leading to the reduction of the external surface area of the zeolites, so fewer AlO_4^- tetrahedrons needed the charge balancing. To conclude, the increasing water content of the gel composition, the decreasing the crystallinity and the bigger the crystal size of as-synthesized zeolites. Optimum molar ratio of H_2O/Al_2O_3 = 70 was confirmed for the highest crystallinity and smallest size of nanocrystals.

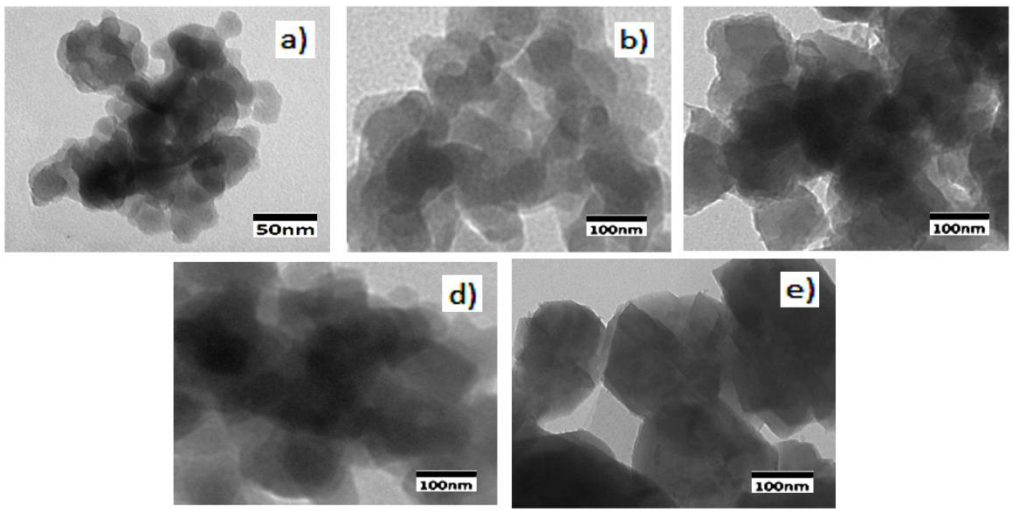


Figure 4. TEM images of Y-70H (a), Y-90H (b), Y-110H (c), Y-130H (d) and Y-150H (e).

Effect of silicon molar ratio on the nanocrystals zeolite NaY: XRD and TEM of as synthesized zeolite Y were shown in Figure 5,6 and table 5. It could be seen that the higher the molar ratio of SiO_2/Al_2O_3 in the gel composition (from 5 to 9), the higher the crystallinities of the as-synthesized zeolites (from 75 % up to 95 %). Accoding to XRD calculations, it was interesting that there was a slightly decrease of the zeolite nanocrystal sizes to 20 nm with SiO_2/Al_2O_3 molar ratio of 7 before the crystal sizes get bigger.

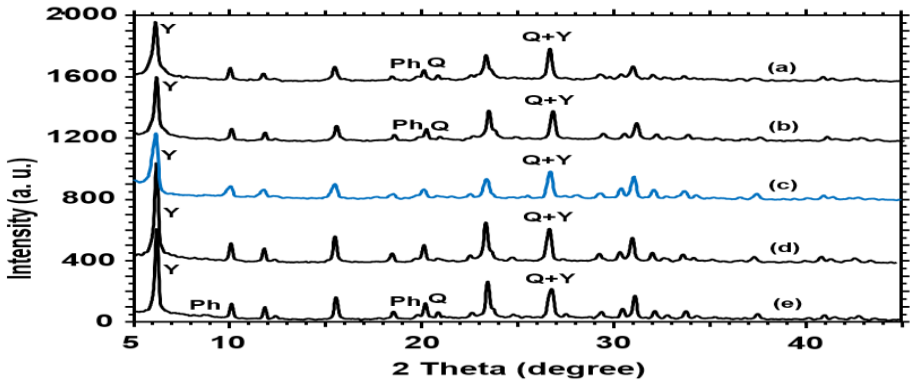


Figure 5. XRD patterns of samples: Y-5S (a), Y-6S (b), Y-7S (c), Y-8S (d) and Y-9S (e). Y: zeolite NaY, Ph: Phlogopite, Q: α-quartz; Q+Y stand for two peaks of two phases of zeolite and α-quartz at the same 2-Theta positions.

The XRD patterns of samples Y-7S and Y-8S also indicated that there was only difference between their peak intensities and peak widths. In this case, the peak intensities of the Y-7S were lower than that of the Y-8S, but the peak widths of the Y-7S were bigger than that of the Y-8S. This illustrated that the crystal sizes of the Y-7S were smaller than that of the Y-8S.

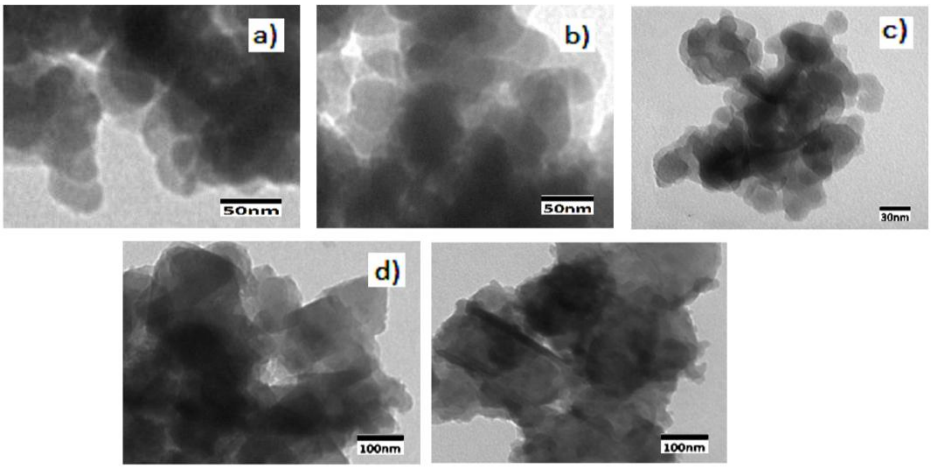


Figure 6. TEM images of samples Y-5S (a), Y-6S (b), Y-7S (c), Y-8S (d) and Y-9S (e).

It could be seen from table 5 that the CECs depended on the crystallinities and the crystal sizes of the as-synthesized zeolites. The higher crystallinity and the smaller crystal sizes led to the higher value of the CECs. In this study, the SiO_2/Al_2O_3 molar ratio of 7 was the optimum ratio to obtain the highest crystallinity of smallest zeolite NaY nanocrystals from Vietnamese kaolin.

Table 5. Effect of silicon molar ratio in the gel on the crystal sizes of zeolite NaY nanocrystals.

No.	Samples	XRD		CEC, mep/100g
		Crystallinities, %	Crystal sizes, nm	
1	Y-5S	75	45	198
2	Y-6S	87	40	217
3	Y-7S	95	20	261
4	Y-8S	95	135	246
5	Y-9S	90	160	225

Effect of alkaline molar ratio in the gel on the nanocrystals zeolite NaY:

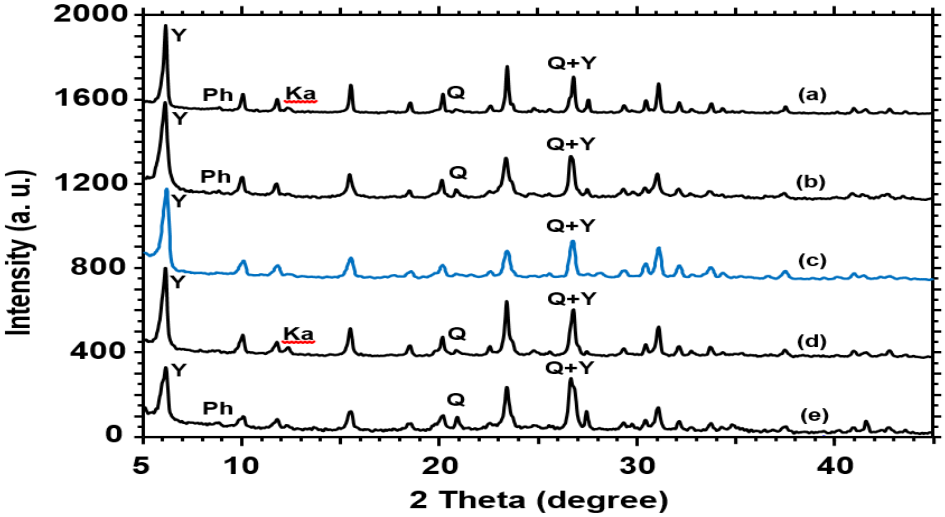


Figure 7. XRD patterns of samples Y-2.5N (a), Y-3.0N (b), Y-3.5N (c), Y-4.0N (d) and Y-4.5N (e).Y: zeolite NaY, Ph: Phlogopite, Ka: Kaolinite, Q: α-quartz; Q+Y stand for two peaks of two phases of zeolite and α-quartz at the same 2-Theta positions.

Figure 7 reported stacked XRD patterns of as-synthesized zeolites NaY with Na_2O/Al_2O_3 molar ratio in the gel from 2.5 to 3.5 (Figure 7a-c). The less favourable conditions for the impurities phase such as Ph, Ka and Q corresponding to Phlogopite, Kaolinite and α-quartz respectivery, were to increasing the Na_2O/Al_2O_3 ratio from 2.5 to 3.5. However, when the ratio increase from 3.5 to 4.5 (Fig. 7c-e), the formation and growth of zeolit NaY were competitive with Ph, Ka and Q phase. Especially, when the ratio reached 4.5, the background of XRD pattern was very high as well as the peak intensity at 2θ = 6,08 was very weak. That was because of a dissolution of the crystal phase of the zeolite NaY due to the excess alkaline. It can be seen that low alkaline concentration was not enough to dissolve impurities and make the secondary building units (SBUs) [2] before the growing of the zeolites NaY, but too high alkaline concentration would dissolve both the impurities and the zeolite crystal phase and formed amorphous phases.

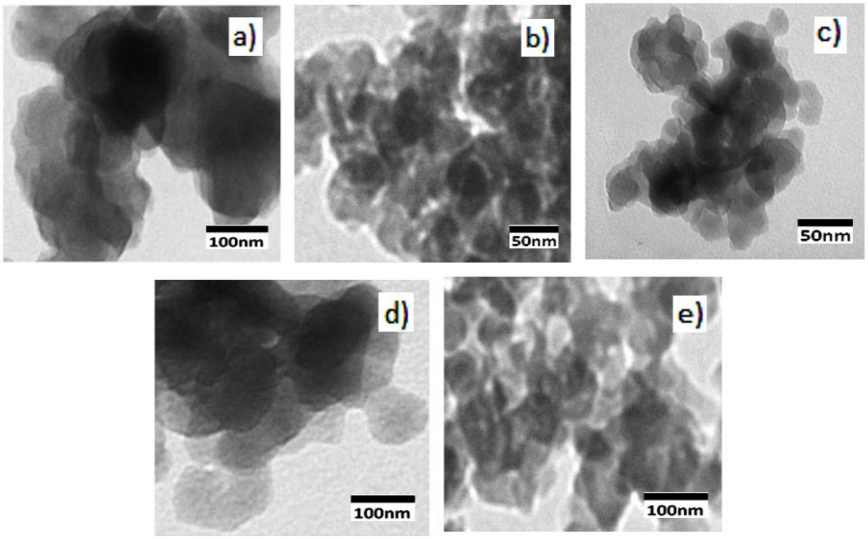


Figure 8. TEM image of samples Y-2.5N (a), Y-3.0N (b), Y-3.5N (c), Y-4.0N (d) and Y-4.5N (e).

The TEM images on figure 8 clear clarified the crystal structure of the zeolites with minimum size of 20 nm similar to the size calculated from XRD patterns. This was also to emphasize that the crystal size distributions were very narrow. The SEM images showed that the crystal morphologies were highly uniform, but their sizes were different when varying the Na_2O/Al_2O_3 ratios in gel compositions.

The sample Y-3.5N synthesized with Na_2O/Al_2O_3 molar ratio of 3.5 had the biggest FWHM value (Full width at half maximum) at 2θ = 6,08^o showing the smallest crystal sizes. According to the calculation based on FWHM and peak intensities on XRD patterns [10], the sample Y-3.5N had the maximum crystallinity (95 %) and minimum crystal size (20 nm) among other samples.

Table 6. Effect of alkaline molar ratio on the nanocrystals zeolite NaY

No.	Samples	XRD		CEC, meq/ 100g
		Crystallinities, %	Crystal sizes, nm	
1	Y-2.5N	85	120	218
2	Y-3.0N	88	45	230
3	Y-3.5N	95	20	261
4	Y-4.0N	90	80	226
5	Y-4.5N	65	87	179

As shown in Table 6, CEC value of the sample Y-3.5N was the largest illustrating the highest crystallinity and the smallest crystal sizes of all other samples. The sample Y-3.5N was considered as the sample contained most of AlO_4^- tetrahedrons and having the largest surface area, so it could give the most cationic exchange performance. The optimum ratios was of 3.5 to generate high crystallinity and small crystal size. In conclusion, when the Na_2O/Al_2O_3 ratios in the gel compositions were too low, it was not enough to dissolve the impurities and build the SBU for the crystalization. On the other hand, if the ratio was too high, both formed crystals and the impurities were dissolved. The suitable Na_2O/Al_2O_3 molar ratio in gel compositions was 3.5 in this study.

Effect of NaCl molar ratio on the nanocrystals zeolite NaY:

Table 7. Effect of NaCl content on the crystal sizes of zeolit NaY nanocrystals

No	Samples	XRD		CEC, Meq $100g^{-1}$
		Crystallinities, %	Crystal sizes, nm	
1	Y-0NaCl	65	180	175
2	Y-1NaCl	80	135	215
3	Y-2NaCl	92	35	230
4	Y-3NaCl	95	20	261
5	Y-4NaCl	80	105	217
6	Y-5NaCl	50	125	120

Characterization of as-synthesized samples with different NaCl molar ration was shown in figure 9,10 and in table 7.

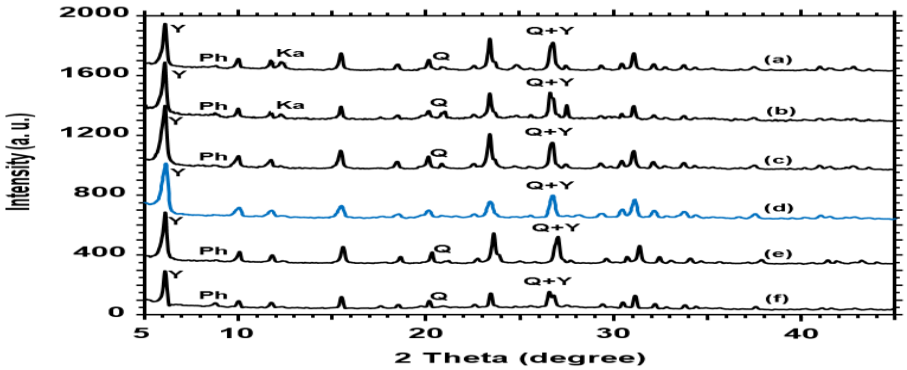


Figure 9. XRD patterns of samples: Y-0NaCl (a), Y-1NaCl (b), Y-2NaCl (c), Y-3NaCl (d), Y-4NaCl (e) and Y-5NaCl (f). Y: zeolite NaY, Ph: Phlogopite, Ka: Kaolinite, Q: α-quartz; Q+Y stand for two peaks of two phases of zeolite and α-quartz at the same 2-Theta positions.

The XRD pattern of sample Y-0NaCl without NaCl revealed the zeolite crystal phases with high peak intensities. However, many impurity peaks were observed assigning for Ph, Ka and Q with considerable intensities. These peaks were caused by the uncompleted transforms of the beginning materials.Varyfing the $NaCl/Al_2O_3$ ratio from 1 to 5 led to different results. Increasing the $NaCl/Al_2O_3$ ratio from 1 to 3 led to a decrease in the impurity XRD peak intensities. Increasing the ratios of 3 to 5, the impurity peak intensities of Ph and Q became stronger. Especially, with a ratio of 5/1 (Fig. 9f), the XRD pattern had a very high background, and the zeolite peak intensities were very low illustrating a large amount of amorphous phase.

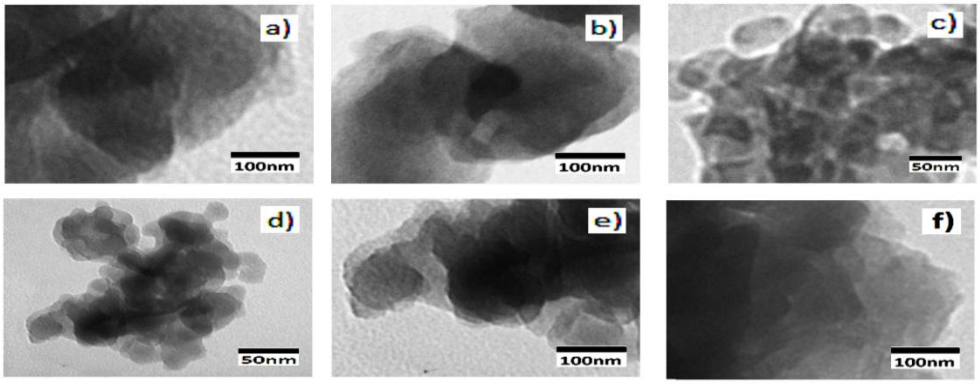


Figure 10. TEM images of samples Y-0NaCl (a), Y-1NaCl (b), Y-2NaCl (c), Y-3NaCl (d), Y-4NaCl (e) and Y-5NaCl (f).

Effect of EDTA molar ratio on the crystal sizes of zeolit NaY nanocrystals:

Table 8. Effect of EDTA molar ratio on the crystal sizes of zeolit NaY nanocrystals

No.	Samples	XRD		CEC, meq $100g^{-1}$
		Crystallinities, %	Crystal sizes, nm	
1	Y-E0.0	10	-	98
2	Y-E0.3	25	-	125
3	Y-E0.6	55	-	170
4	Y-E0.9	80	45	212
5	Y-E1.2	95	20	261
6	Y-E1.5	85	135	217
7	Y-E1.8	70	-	190

The XRD patterns of 7 studied samples with various EDTA/Al_2O_3 molar ratios in gel compositions (from 0 to 1.8 with steps of 0.3) were described in figure 11. The crystallinity, crystal size and CEC calculations were described in table 8.

When the EDTA/Al_2O_3 molar ratio increased, the crystallinity of all samples increased and got a maximum at the ratio of 1.2. Then the crystallinity tended to be decreased when the EDTA/Al_2O_3 was kept increasing. The XRD patterns of the samples from Y-E0.0 (Fig. 11a) to Y-E0.6 (Fig.11c) contained many impurities such as Ha, Q or amorphous phases. Other sample showed less impurities, partially by transforming the Ha phase to Ph phase (Ph – Phlogopit, PDF 02-0053). The Ha (Halloysite, PDF 029-1489) was an amorphous material of kaolin mineral with high thermal and hydrothermal stabilities.

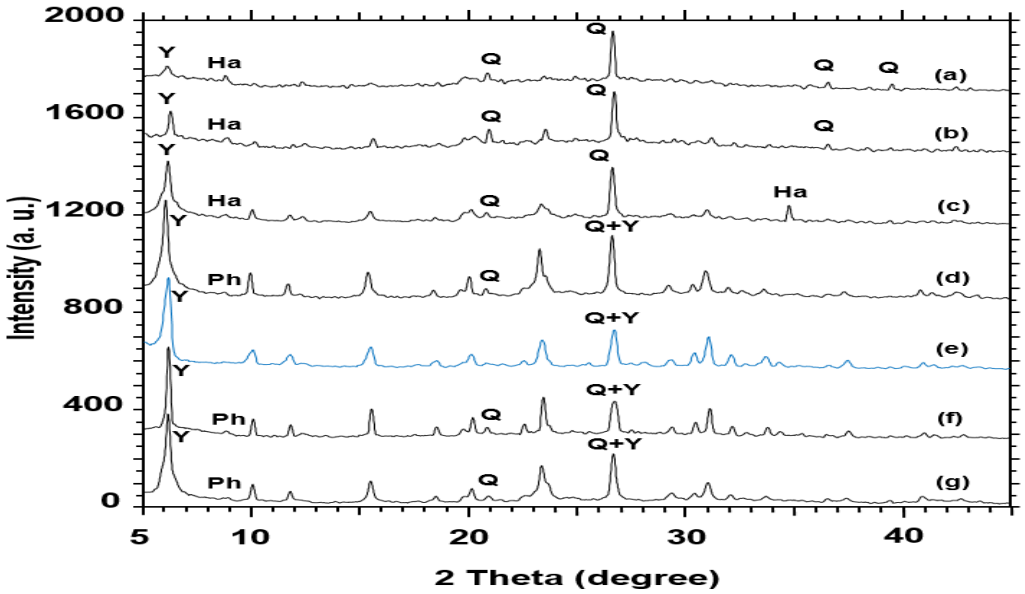


Figure 11. XRD patterns of samples: Y-E0.0 (a), Y-E0.3 (b), Y-E0.6 (c), Y- E0.9 (d), Y- E1.2 (e), Y- E1.5 (f) and Y- E1.8 (g). Y: zeolite NaY, Ph: Phlogopite, Ha: Halloysite, Q: α-quartz; Q+Y stand for two peaks of two phases of zeolite and α-quartz at the same 2-Theta positions.

The sample Y-E1.8 (Fig. 11g) showed a considerable background demonstrating partial destruction of zeolite NaY nanocrystals after formation. Another reason for this high background was the low velocity of transforming and crystallizing Al_2O_3 and SiO_2 from amorphous to crystal phase. The TEM and SEM images in Fig. 12 showed the uniform distribution of particles in 3 high crystallined samples Y-Eq (q = 0.9; 1.2 and 1.5). The minimum crystal sizes observed from TEM were 20 nm with EDTA/Al_2O_3 molar ratio of 1.2. The relation between crystal and partical size similar to the result dicussed in part 3.1.

Table 8 indicated when the EDTA/Al_2O_3 molar ratio was low, there were not enough nucleations attracting the TO_4 tetraherdons (T assigned for Al and Si) to form the D6R-SBUs, so the crystallinity of the zeolites was low. When the EDTA/Al_2O_3 ratio was too high, it might occur a competition between stable Al^{3+} coordinators, so it was more difficult for the Al^{3+} cation to build the AlO_4^- tetrahedrons. These led to the decreasing of the zeolite crystallinity.

The optimum EDTA/Al_2O_3 ratio for maximum crystallinity and smallest crystal size of the as-synthesized zeolite was 1.2. This explanation was confirmed by the CEC determinations of the samples in Tab. 8. The sample Y-E1.2 had a highest CEC value illustrating the maximum amount of AlO_4^- tetrahedrons or the highest crystallinity and smallest crystal size. Using EDTA was required in the synthesis of zeolite NaY nanocrystals as Al-complexing agent, modulating the concentration of reactive aluminum, and thus a tool to control their crystal sizes. The optimum ratio of EDTA/Al_2O_3 in the gel composition was 1.2.

Effects of synthetic parameters on the bulk density of zeolit NaY nanocrystals:

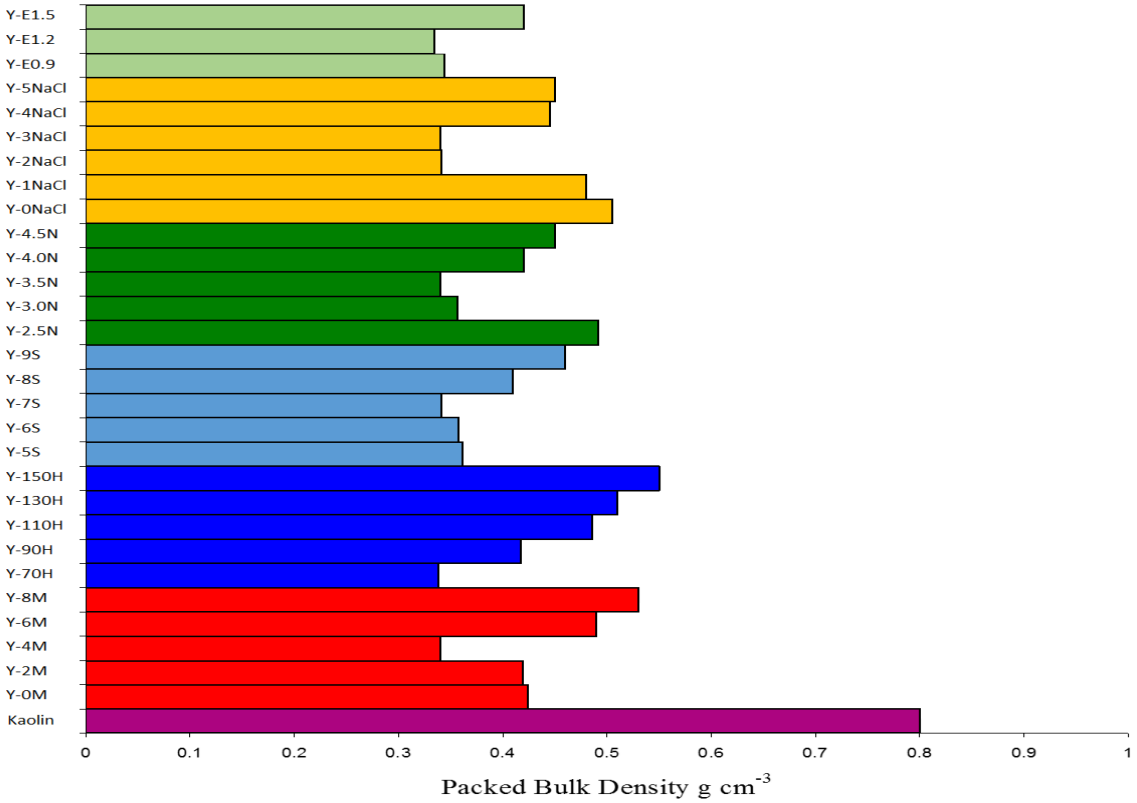
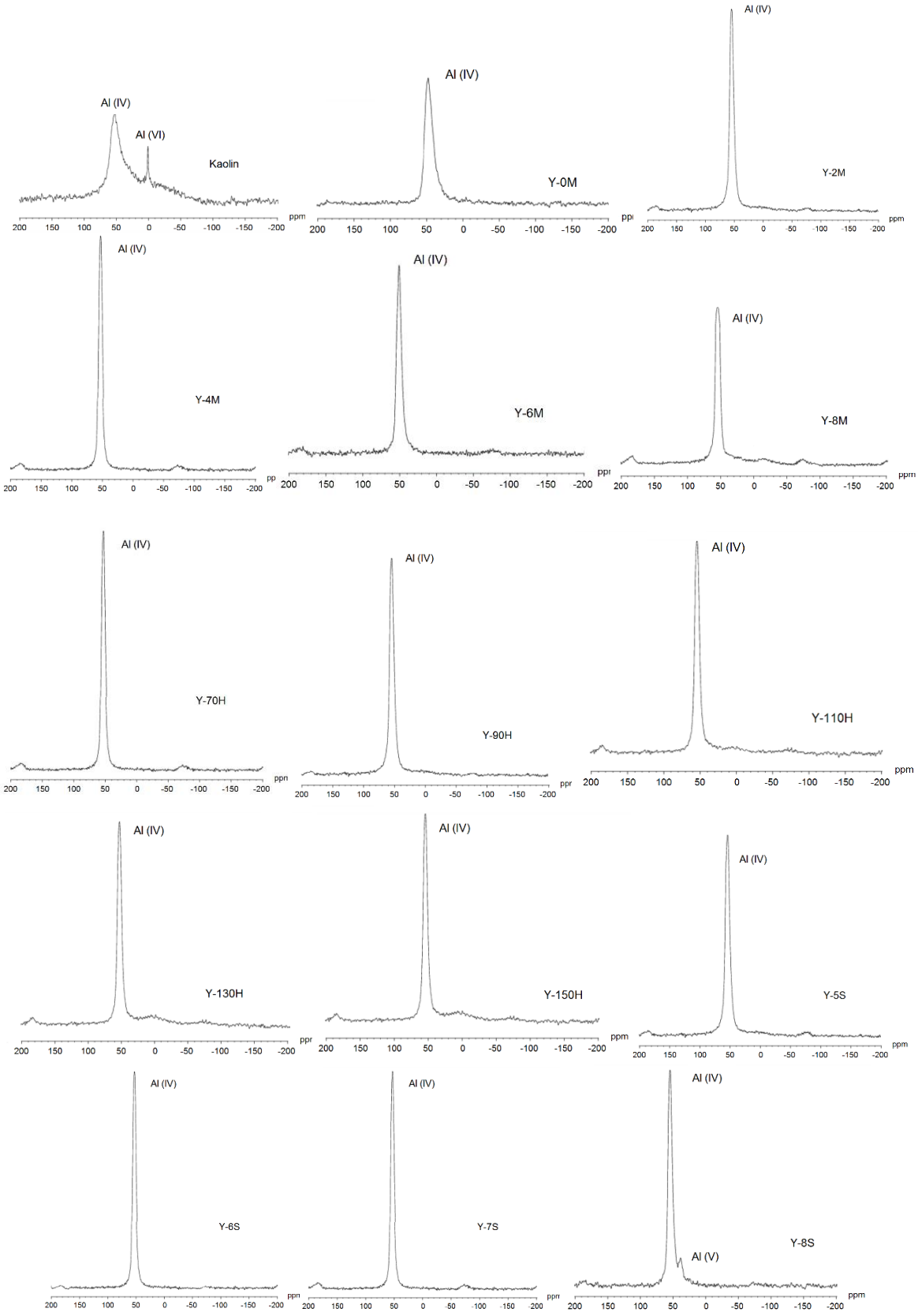


Figure 12: Packed bulk density for raw Kaolin and as-synthesized zeolite Y samples.

The average bulk density of raw Vietnamese Kaolin (Figure 12) was ~ 0.8 g cm^{-3}, similar to other kaolin type has been reported [10]. In general, Kaolin precursor was much denser than the corresponding zeolite NaY materials (from 0.32-0.55 g cm^{-3}). The average bulk density (determined by using the ASTM D6683 – 14) of the zeolite Y materials was close to the values reported in the literature (0.54 g cm^{-3}) [10-12]. It was hypothesised that the lower density of the crystalline materials was due to the more ordered nature of the materials. Although all of the materials produced were porous, the repeating unit cell and reportedly larger pore dimensions of the crystalline materials results in them being less dense.

It was clearly that the crystal size strongly related to the bulk density. The smaller the crystal size, the less dense the as-synthesized materials. That meant which synthetic parameters had strong effects on the crystal size of zeolite Y would also have strong effects on the bulk density. Only in the case of H_2O molar ratio in the gel, the higher the ratio the denser the material. With other synthetic parameters, optimum condition to obtain the smallest crystal size would create the material with the smallest bulk density. The sample synthesized from kaolin treated with HCl 4M, with the molar ratio H_2O/Al_2O_3 = 70, SiO_2/Al_2O_3=7, Na_2O/Al_2O_3 =3.5, $NaCl/Al_2O_3$ = 3, $EDTA/Al_2O_3$=1.2 with crystal size of 20nm had the lowest bulk density of 0.34 gcm^{-3}.

Effects of synthetic parameters on the nature of aluminium sites in the structure zeolit NaY nanocrystals:


Al (IV)
Al (VI)
Kaolin
Y-0M
Y-2M
Y-4M
Y-6M
Y-8M
Y-70H
Y-90H
Y-110H
Y-130H
Y-150H
Y-5S
Y-6S
Y-7S
Y-8S
Al (V)
ppm

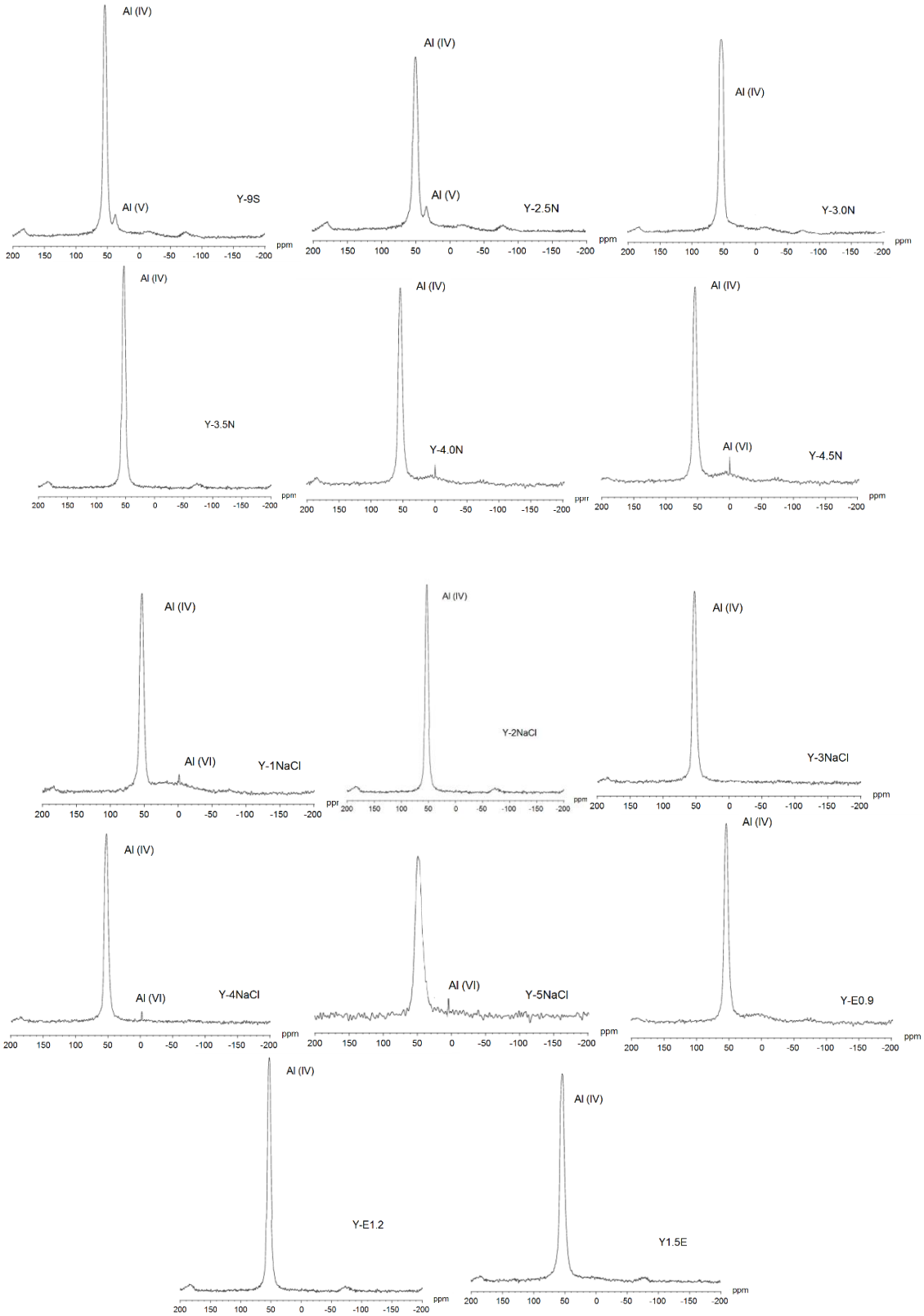


Figure 13: ^{27}Al NMR spectra of raw kaolin and as-synthesized zeolite NaY

The bonding environment of the aluminium cannot be deduced from UV-vis analysis, thus ^{27}Al NMR data was collected for all of the aluminium containing materials (Figure 13). Three possible signals were expected for zeolite materials, two of them at approximately 60, and 0 ppm which were assigned to tetrahedral and octahedral coordinate aluminium respectively [13,14]. The third predicted peak at ~ 30 ppm has been reportedly assigned either as aluminium in AlO_5 polyhedra or as distorted AlO_4 tetrahedra [15].

The NMR data collected from raw kaolin and as-synthesized zeolites were shown in figure 13. In general, which material exhibited one sharp signal at ~ 50 ppm attributed to tetrahedral coordinated aluminium heteroatoms would have more ordered structure than others exhibited wide signal of signal at ~ 50 ppm or ~ 30 ppm attributed to octahedral and distorted coordinated aluminium. NMR of raw kaolin exhibited two signal at at ~ 50 ppm and 0 ppm attributed to tetrahedral and octahedral coordinated aluminium in its structure. This was absolutely different from all other zeolite Y sample, showing the much more ordered structure in as-synthesized materials. Almost all as-synthesized zeolite showed predominate narrowed signal at ~ 50 ppm. Some of them contained an additional minor peak at around ~ 30 ppm or 0 ppm. The presence of two peaks would have been indicative of two crystallographic distinct aluminium sites within the silica lattice. The NMR spectra of the zeolite materials allowed prediction of the most beneficial catalysts, those materials whose NMR spectra depicted all of the aluminium centres to be in tetrahedral sites were proposed to be more catalytically reactive.

Zeolite Y materials Y-4M, Y-70H, Y-7S, Y-3.5N, Y-3NaCl, Y-E1.2 produced NMR spectra which exhibited the narrowest sole peak of all the materials examined, indicative of them being the most crystalline and with solely tetrahedral aluminium centres. The signals produced from Y 2.5N, Y- 4.0N, Y-4.5N, Y-4NaCl, Y-5NaCl, Y-9S had a principal peak at ~ 50 ppm and a slight peak at ~ 0 ppm which suggested that whilst the majority of the aluminium heteroatoms were tetrahedrally coordinated a minority were in octahedral or pentahedral/ distorted tetrahedral sites. The material with only tetrahedral aluminium sites was expected more potential for catalytic reactivity than those with extra signals.

Thus it could be seen from NMR data that some of synthetic parameters such as SiO_2/Al_2O_3, Na_2O/Al_2O_3 and $NaCl/Al_2O_3$ had strong effects on the nature of aluminium sites, but other did not. In the case of SiO_2/Al_2O_3, best ratio was of 6-7 to generated most crystalline materal with solely tetrahedral aluminium sites. When the SiO_2/Al_2O_3 increased to 8-9, it also generated pentahedral/ distorted tetrahedral sites, assigned to ~ 30 ppm signal. Na_2O/Al_2O_3 and $NaCl/Al_2O_3$ ratio in the synthetic gel had similar effects on the nature of aluminium sites in as-prepared zeolites. Too low or too high ratio would generate additional minor peaks in NMR at ~ 0 ppm caused by aluminium centres at octahedral coordinations. NMR data were well agreed with TEM, XRD, chemical compositions and bulk density that that best conditions to obtain smallest nanocrystal with high crystalline and solely tetrahedral aluminium coordination was H_2O/Al_2O_3 = 70, SiO_2/Al_2O_3=7, Na_2O/Al_2O_3 =3.5, $NaCl/Al_2O_3$ = 3, $EDTA/Al_2O_3$=1.2.

NMR of samples synthesized with different HCl,H_2O, EDTA molar ratio were similar, exhibited only one peak at ~ 50 ppm either narrow or a little broader. This illustrated that HCl, H_2O and EDTA molar ratio had strong effects on the crystal size of nano zeolite Y but did not have strong effects on the nature of aluminium sites in the zeolite structures.

Other properties of as-synthesized NaY nanocrystals: Others structural information can be obtained from the vibrational frequencies of the zeolite lattice observed in the range between 400 and 1,300 cm^{-1}. The FT-IR spectra of zeolite NaY nanocrystals (Y-4M) is exhibited in figure 14.

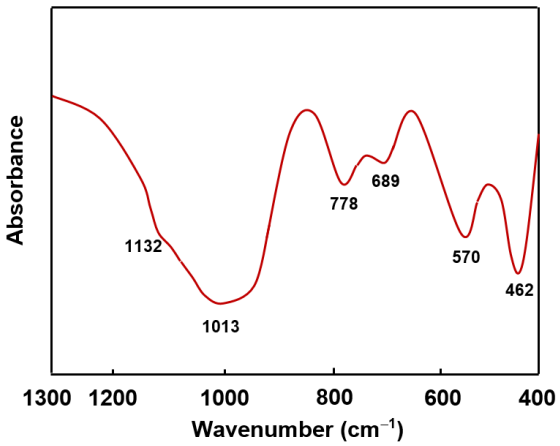


Figure 14. FT-IR zeolite NaY nanocrytals

The peak at 462 cm^{-1} is assigned to the structure insensitive internal TO_4 (T = Si or Al) tetrahedral bending peak of zeolite NaY. The peak at 570 cm^{-1} is attributed to the double ring external linkage peak. The peaks at 689 and 778 cm^{-1} are assigned to external linkage symmetrical stretching and internal tetrahedra symmetrical stretching, respectively. The peaks at 1013 and 1132 cm^{-1} are assigned to internal tetrahedral asymmetrical stretching and external linkage asymmetrical stretching, respectively. Overall, the FT-IR spectra matched well with the characteristic zeolite NaY nanocrystals absorption peaks in other studies [17, 18].

The element analysis of the zeolite exhibited the SiO_2/Al_2O_3 molar ratio of 3.93 showing a small amount of SiO_2 in the impurity phase phlogopite existed from the precursor materials. The N_2 adsorption–desorption isotherms and pore distribution of the zeolite NaY nanocrystals (Y-4M) are given in Fig. 15. In N_2 sorption isotherms, the sample showed a steep uptake at very low relative pressures corresponding to the filling of micropores (Fig. 15a). There was a hysteresis curve started at P/Po about 0.6 matching to style IV in the pore classification [19]. This was caused by a nitrogen condensation in the mesopores. For the as-synthesized nano zeolite Y, the mesopores were generated by the secondary arrangement of the nanosized crystals.

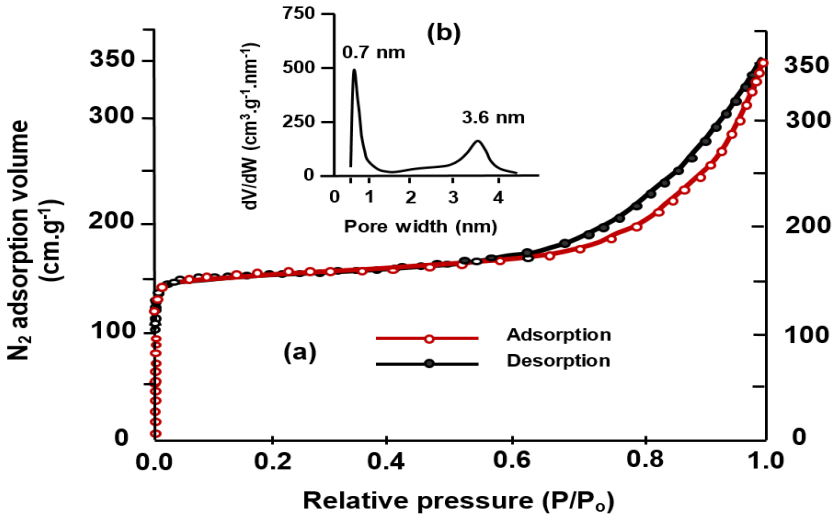


Figure 15. N_2 adsorption-desorption isotherms (a) and pore distribution (b) of zeolite NaY nanocrystals

The sample exhibited a BET surface high area of 615 m^2/g. It was noted that micro-sized crystals usually exhibited an external surface area < 5 m^2/g [20] and nano-sized (48 nm) had BET surface area of around 87 m^2/g [18]. In our case, the external surface area of sample was calculated to be 126 m^2/g, which was consistent with the expected value. A micropore volume (0.17 cm^3/g) was determined by the *t*-plot method. The mesopore volume of the samples was estimated to be 0.19 cm^3/g, and the average pore diameter was determined to be 2.1 nm using BJH method (Fig. 15b). It also contained both micropores and mesopores with the pore widths of 0.7 nm and 3.6 nm, respectively.

CONCLUSIONS

Various parameters afftecting the preparation of the zeolite NaY nanocrystals from Vietnamese kaolin were studied. The results showed that all synthetic parameters somehow affected the crystal size of nano zeolite Y but at different level. The water content in the gel compositions increased, the crystallinity decreased with a sharply increase of crystal sizes. When the Na_2O/Al_2O_3 ratio in the gel is too low, it is not a favourable environment for the dissolution of precursors and create SBU for the crystallization of zeolite NaY nanocrystals. But if the ratio of Na_2O/Al_2O_3 is too high it partially dissolve the generated nanosized crystals. The optimum molar ratio of Na_2O/Al_2O_3 in this study was 3.5 to obtain smallest nanocrystal NaY. EDTA was required in the synthesis of zeolite NaY nanocrystal as the template and a tool to control their partical sizes. Introducing NaCl into the gel compositions were recommended because it accelerated the electrolyte of the reaction system and added an extra cations Na^+ for balancing the negative charges of the AlO_4^- tetrahedrons. Then the high crystallinity and small size crystals were conveniently generated. Bulk density and NMR data agreed with other characterization that which synthetic parameters had strong effects on the crystal size of zeolite Y would also have strong effects on the bulk density. The smaller the nano crystal sizes, the lower the bulk density. NMR confirmed that HCl, H_2O and EDTA molar ratio had strong effects on the crystal size of nano zeolite Y but did not have strong effects on the nature of aluminium sites in the zeolite structures.

In suitable conditions of the preparation with H_2O/Al_2O_3 = 70, SiO_2/Al_2O_3=7, Na_2O/Al_2O_3 =3.5, $NaCl/Al_2O_3$ = 3, $EDTA/Al_2O_3$=1.2, zeolite NaY nanocrystals were synthesized with highest crystallinity of 95 %, lowest bulk density of 0.34 gcm^{-3}, surface area of 615 m^2/g including external area of 126 m^2/g, pore distributions of 0.7 nm and 3.6 nm, the crystal size was about 20 nm and contained solely tetrahedral aluminium sites in the structure.

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