Synthesis, characterization and application of nanozeolite NaX from Vietnamese kaolin

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Abstract
This paper presents the results of synthesis of nanozeolite NaX from Vietnamese kaolin. Influence factors on the control of crystal sizes and application of synthesized materials as adsorbent for organic compound are discussed. The results show that there are several factors that influence the synthesis. When water content in gel increases, crystal size of NaX increases sharply. The increase of alkaline and silica contents increases the crystallinity and decreases the particle size of nano NaX, and the particle size reaches the minimum at Na₂O/Al₂O₃ = 5.0 and SiO₂/Al₂O₃ = 4.0. Crystal sizes formed at low crystallizing temperature are smaller than those formed at higher temperature. Ageing time and crystallizing time strongly influence the crystallinity and crystal size, which is related to the number of crystal seeds formed during ageing period, the growth of seed and the partial solubility of crystal at maximum formation. Nano NaX was characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) adsorption, Fourier transform infrared (FTIR) and simultaneous thermogravimetry–differential scanning calorimetry (TG/DSC). At optimized synthesis conditions, nano NaX has surface area of 573 m² g⁻¹ with external surface area of 92 m² g⁻¹, pore size distribution at 0.81 and 10.8 nm, average crystal size of 25 nm and thermal stability up to 789 °C. This material can adsorb cumene rapidly with high adsorption capacity and stability.

Keywords: nanozeolite, zeolite, kaolin, adsorption

Classification numbers: 4.02, 4.03, 5.18

1. Introduction

Nanoscience and nanoporous materials are currently attracting attention from many scientists. Microporous materials with nanometer particle size (nanozeolites) are being studied because of their outstanding properties that could not be found in the micrometer zeolites.

Reducing the particle size from micrometer to nanometer scale leads to a significant change of material characteristics and their applications in catalysis and adsorption. The number of atoms in the unit cell increases when particle sizes decrease and nanozeolites have large external surface area. The diffusion path length in nanozeolites is shortened as compared to that in the conventional micrometer zeolites.

Most recent research papers about nanozeolite NaX are from pure, expensive chemicals containing organic aluminum and silicium (such as aluminum isopropoxide, tetraethyl orthosilicate- TEOS) and organic templates (tetramethylammonium hydroxide TMAOH, tetramethylammonium bromide TMABr) in alkaline media in certain synthetic conditions [1–4]. Nanozeolites with crystal
Table 1. Molar composition and crystallizing condition.

| No. | Code      | Crystallizing temperature  (°C) | Na\(_2\)O/Al\(_2\)O\(_3\) | SiO\(_2\)/Al\(_2\)O\(_3\) | H\(_2\)O/Al\(_2\)O\(_3\) | Ageing time (h) | Crystallizing time (h) |
|-----|-----------|--------------------------------|---------------------------|---------------------------|------------------------|-----------------|------------------------|
| 1   | X96-12-60 | 60                            |                           |                           |                        | 70              | 96                     | 12                     |
| 2   | X96-12-80 | 80                            | 5                         | 4                         | 70                     |                 |                        |                        |
| 3   | X96-12-100| 100                           |                           |                           |                        |                 |                        |                        |
| 4   | X96-12-2N | 2                             |                           |                           |                        |                 |                        |                        |
| 5   | X96-12-3N | 3                             |                           |                           |                        |                 |                        |                        |
| 6   | X96-12-4N | 80                            | 4                         | 4                         | 70                     | 96              | 12                     |
| 7   | X96-12-5N | 5                             |                           |                           |                        |                 |                        |                        |
| 8   | X96-12-6N | 6                             |                           |                           |                        |                 |                        |                        |
| 9   | X96-12-7N | 7                             |                           |                           |                        |                 |                        |                        |
| 10  | X96-12-3.0S| 3.0                           |                           |                           |                        |                 |                        |                        |
| 11  | X96-12-3.5S| 3.5                           |                           |                           |                        |                 |                        |                        |
| 12  | X96-12-4.0S| 80                            | 5                         | 4.9                       | 70                     | 96              | 12                     |
| 13  | X96-12-4.5S| 80                            | 4.5                       |                           |                        |                 |                        |                        |
| 14  | X96-12-5.0S| 5.0                           |                           |                           |                        |                 |                        |                        |
| 15  | X96-12-70H | 70                            |                           |                           |                        |                 |                        |                        |
| 16  | X96-12-90H | 90                            |                           |                           |                        |                 |                        |                        |
| 17  | X96-12-110H| 110                           |                           |                           |                        |                 |                        |                        |
| 18  | X96-12-130H| 130                           |                           |                           |                        |                 |                        |                        |
| 19  | X96-12-3.0S| 3.0                           |                           |                           |                        |                 |                        |                        |
| 20  | X24-12    | 24                            |                           |                           |                        |                 |                        |                        |
| 21  | X48-12    | 48                            |                           |                           |                        |                 |                        |                        |
| 22  | X72-12    | 80                            | 5                         | 4                         | 70                     | 72              | 12                     |
| 23  | X96-12    | 96                            |                           |                           |                        |                 |                        |                        |
| 24  | X120-12   | 120                           |                           |                           |                        |                 |                        |                        |
| 25  | X144-12   | 144                           |                           |                           |                        |                 |                        |                        |
| 26  | X96-06    | 6                             |                           |                           |                        |                 |                        |                        |
| 27  | X96-12    | 80                            | 5                         | 4                         | 70                     | 96              | 12                     |
| 28  | X96-18    | 18                            |                           |                           |                        |                 |                        |                        |
| 29  | X96-24    | 24                            |                           |                           |                        |                 |                        |                        |
| 30  | Micro-NaX | 95                            | 4                         | 4                         | 160                    | 72              | 24                     |

size of 75 nm were synthesized in 168 h at 100 °C and those of 137 nm were synthesized in 72 h at 130 °C [1]. Ultra-fine NaX zeolite crystals with dimensions of 23 nm were synthesized in 48 h at 90 °C [2]. The conversion of amorphous gel in 22 days at room temperature formed nanoparticles with crystal size of 20 nm [3]. Mesoporous NaX zeolites with sizes of 4–50 nm were synthesized by using organic templates of cationic polymer (polydiallyldimethylammonium chloride, PDADMAC) at 100 °C in 16 h [5]. Limited studies have reported the synthesis of nanozeolite ZSM-5 from kaolin [6], and to our knowledge nanozeolite NaX synthesized from kaolin has not been reported in literature.

This paper presents the results of synthesis of nanozeolite NaX from Vietnamese kaolin. The factors influencing the control of particle sizes and application of synthesized materials as adsorbent for organic compound are discussed.

2. Experimental

2.1. Synthesis of nanozeolite NaX

Vietnamese kaolin was heated at 600 °C in 3 h and a metastable phase referred to as metakaolin was obtained. Metakaolin was mixed with liquid glass, sodium hydroxide, distilled water, EDTA and sodium chloride. The molar composition of initial gel was \( aNa_2O \cdot Al_2O_3 \cdot bSiO_2 \cdot cH_2O \cdot 1.2EDTA \cdot 2NaCl \) (whereas \( a = 2–7, \ b = 3–5, \ c = 70–130; \) EDTA/Al\(_2\)O\(_3\) = 1.2 and NaCl/Al\(_2\)O\(_3\) = 2) [7]. The obtained solutions were aging at room temperature in 24–144 h and hydrothermal crystallized at 60–100 °C in 6–24 h in autoclave at autogenous pressure.

Micrometer zeolites NaX (noted as micro-NaX) were synthesized with procedure in [8] for the comparison. 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 9. Nanoparticles were dried at 110 °C and calcined at 550 °C.
Figure 2. SEM images of nanozeolites NaX crystallized at 60 °C (a), 80 °C (b) and 100 °C (c).

Figure 3. TEM images of nanozeolites NaX crystallized at 60 °C (a), 80 °C (b) and 100 °C (c).

Table 2. Influence of temperature on the crystallization of nanozeolite NaX.

| No. | Sample code | Crystallizing temperature (°C) | Crystallinity by XRD (%) | Average crystal size (nm) |
|-----|-------------|-------------------------------|--------------------------|--------------------------|
| 1   | X96-12-60   | 60                            | 50                       | 42  | 50  | 68  |
| 2   | X96-12-80   | 80                            | 92                       | 25  | 32  | 54  |
| 3   | X96-12-100  | 100                           | 72                       | 128 | 150 | 354 |

2.2. Characterization

XRD analyses were carried out at room temperature in θ–2θ reflection mode using a SIEMENS D5005 diffractometer. SEM and TEM images were obtained on JSM 5410 LV and JEM 1010. Specific surface area determinations (BET) and pore size distributions were measured on a COULTER SA3100 apparatus. FTIR was performed on Nicolet impact FTIR 410 Spectrometer. TG/DSC was performed on NETZSCH STA 409 PC/PG.

Cumene adsorption was performed at 40 °C in dynamic mode. Nitrogen, with a purity of 99.99%, was used as the carrier gas. N₂ was conducted to the pre-saturator containing pure liquid cumene before sending through adsorbent bed. The concentration of xylene vapor in the inlet was 5200 ppm. Before adsorption measurements, adsorbents were out-gassed at 423 K for 1–3 h. The cumene in gas flow was analyzed by GC-14B Shimadzu online.

3. Results and discussion

3.1. Influence of crystallizing temperature

XRD patterns, SEM and TEM images of nanozeolites NaX synthesized at different temperature are shown in figures 1, 2 and 3, respectively. Other results are listed in table 2.
Figure 5. SEM images of X96-12-2N (a), X96-12 -3N (b), X96-12-4N (c), X96-12-5N (d), X96-12-6N (e) and X96-12-7N (f).

Figure 6. TEM images of sample X96-12-2N (a), X96-12 -3N (b), X96-12-4N (c), X96-12-5N (d), X96-12-6N (e) and X96-12-7N (f).

Table 3. Influence of alkaline content on the crystallization of nanozeolite NaX.

| No. | Sample code | Ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ in gel | Crystallinity by XRD (%) | Average crystal size (nm) |
|-----|-------------|-------------------------------------------------|---------------------------|---------------------------|
|     |             |                                                 |                           | By XRD | By TEM | By SEM |
| 1   | X96-12-2N   | 2                                               | 80                        | 101    | 120    | 147    |
| 2   | X96-12-3N   | 3                                               | 82                        | 93     | 100    | 120    |
| 3   | X96-12-4N   | 4                                               | 86                        | 70     | 75     | 90     |
| 4   | X96-12-5N   | 5                                               | 92                        | 25     | 32     | 54     |
| 5   | X96-12-6N   | 6                                               | 90                        | 55     | 62     | 75     |
| 6   | X96-12-7N   | 7                                               | 88                        | 75     | 80     | 96     |
The rise of XRD baselines and SEM and TEM images of samples crystallized at 60 and 100°C prove that there are more amorphous phases on these samples than on a sample crystallized at 80°C and the crystallinity of these samples is low. Crystal sizes of nanolele NaX crystallized at 80°C are the smallest (about 32 nm by TEM).

At low crystallizing temperature (60°C), the crystallizing rate is slow that leads to the low crystallinity of the samples and vice versa, at high crystallizing temperature (100°C), the crystallizing rate is large, so obtained samples have larger crystal size.

3.2. Influence of alkaline content

XRD patterns, SEM and TEM images of nanolele NaX synthesized with different ratios of Na₂O/SiO₂ in gel are shown in figures 4, 5 and 6, respectively. Other results are listed in table 3.

The XRD patterns of all nanolele NaX show the crystalline phase of zeolite NaX and α-quartz with different intensities. When the ratio of Na₂O/SiO₂ in gel increases, the peak intensity of NaX increases and reaches the maximum result at ratio of Na₂O/SiO₂ in gel of 5 (sample X96-12-5N—figure 4(d)), while the peak intensity of quartz decreases and gets the minimum result at this ratio. Sample X96-12-5N also has the largest FWHM.

All the results show that sample X96-12-5N has the highest crystallinity (92%) and smallest crystal size (25 nm calculated from XRD result, see table 3). SEM and TEM images of sample X96-12-5N show the average crystal sizes of 54 nm and 32 nm, respectively.

OH⁻ is mineralizing agent that stimulates the formation of AlO₄⁻ and SiO₄ tetrahedral that are suitable for the crystallization of zeolite NaX. Increasing ratio of Na₂O/Al₂O₃ in gel from 2 to 5 will increase OH⁻ contents, but if the OH⁻ content is too high (Na₂O/Al₂O₃ ratio in gel > 5), AlO₄⁻ tetrahedral are partly dissolved, so the crystallinity decreases and quartz contents increase. The highest crystallinity and smallest crystal size of sample X96-12-5N prove that ratio of Na₂O/Al₂O₃ in gel of 5 is the most suitable to synthesize nanolele NaX.

SEM and TEM images are totally corresponding to the results obtained from XRD patterns.

3.3. Influence of silica content in gel

Figure 7 shows XRD patterns of nanolele NaX with different SiO₂/Al₂O₃ ratios in gel. Sample X96-12-4.0S shows that the intensity of zeolite NaX phase at 2θ = 6.2 is the highest and that of quartz at 2θ = 26.7° is the lowest.

This sample has the highest crystallinity (92%). Full-width at half-maximum (FWHM) of zeolite NaX phase at 2θ = 6.2 is the largest. The crystal size calculated by Scherrer equation is the smallest (25 nm). The framework SiO₂/Al₂O₃ ratio of NaX is 2.5, whereas the SiO₂/Al₂O₃ ratio in gel to crystallize nanolele with high crystallinity is 4, so excess silica content in gel is needed in the preparation of nanolele NaX (table 4).

SEM and TEM images were shown in figures 8 and 9. Sample X96-12-4.0S has the smallest average crystal size of 54 nm (by SEM) and 32 nm (by TEM).

3.4. Influence of H₂O/Al₂O₃ ratio in gel

XRD patterns of nanolele NaX with different water contents in gel are presented in figure 10. The intensities of zeolite NaX crystalline phase increase, the FWHMs decrease when H₂O/Al₂O₃ ratios in gel increase. So increasing the water content in gel leads to the increase of crystal size. FWHM of zeolite NaX crystalline phase measured from XRD pattern and crystal size calculated by Scherrer equation are listed in table 5.

H₂O/Al₂O₃ ratios in gel increase from 70 to 90, crystal size of zeolite NaX increases gradually and are still in nanometer scale, but when it increases from 110 to 130, crystal sizes are in micrometer scale.

Other experiments were also carried out with H₂O/Al₂O₃ ratio in gel < 70. However, the gels were very viscous so that
Figure 8. SEM images of X96-12-3.0S (a), X96-12-3.5S (b), X96-12-4.0S (c), X96-12-4.5S (d) and X96-12-5.0S (e).

Figure 9. TEM images of X96-12-3.0S (a), X96-12-3.5S (b), X96-12-4.0S (c), X96-12-4.5S (d) and X96-12-5.0S (e).

3.5. Influence of aging time

XRD patterns, SEM and TEM images of nanozeolites NaX synthesized with different aging times are shown in figures 11, 12 and 13, respectively. Other results are listed in table 6.

When the ageing time increases, the crystallinity increases and reaches the maximum after 96h, and then decreases slowly. The crystal size also reaches the minimum...
and crystallizing time is long, the crystal phase can be transformed if the crystallizing temperature leads to the low crystallinity. When the aging time is too long (>96 h), many crystal seeds are formed but the phase transformation could occur to form \( \alpha \)-quartz and amorphous alumina that leads to the low crystallinity.

3.6. Influence of crystallizing time

In these experiments the optimal crystallizing temperature of 80°C and aging time of 96 h were used. Influences of crystallizing time have been shown in figures 14, 15 and 16 and table 7.

The crystallinity (by XRD) increases sharply when increasing crystallizing time from 6 to 12 h and then decreases gradually with time on stream.

When crystallizing time is short (<12 h), the crystals are not formed completely so the crystallinity is low. If the crystallizing time is long, the crystal phase can be transformed to stable \( \alpha \)-quartz, so the crystallinity is also decreased. The increase of \( \alpha \)-quartz phase can be observed at 2\( \theta \) = 16.7°.

Average crystal sizes obtained from XRD, SEM and TEM are similar (table 7). Sample X96-12 has the smallest crystal size. The crystallizing time of 12 h is the most suitable for synthesizing nanozeolite NaX.

3.7. Comparison of nanozeolite NaX (nano-NaX) and conventional micro-zeolite NaX (micro-NaX)

XRD patterns of nano- and micro-NaX are shown in figure 17. Zeolite NaX phase (Na\(_2\)O·Al\(_2\)O\(_3·2.5\)SiO\(_2·6.2\)H\(_2\)O, JCPDS 38-0237) appears in both samples. However, micro-NaX shows a very sharp and high intensity peak. Line broadening in nano-NaX is due to the fact that the crystal sizes of nano-NaX are smaller than that of conventional micro-NaX. Analysis of XRD line broadening using the Scherrer equation gives crystal size of nano-NaX of about 19 nm and that of micro-NaX of 0.4 \( \mu \)m.

SEM and TEM images of nano- and micro-NaX are shown in figure 18. Nano- and micro-NaX are in cubic form. Average crystal size of nano-NaX measured from TEM image (figure 18(c)) is 32 nm.

FTIR spectra of micro- and nano-NaX are shown in figure 19. All key bands of nano-NaX resemble those exhibited by micro-NaX, however, the intensities of absorption bands of micro-NaX are stronger. The weak absorption band observed around 608 cm\(^{-1}\) in curve (b) of figure 19 is similar to that of [1], this absorption band only appears on nanozeolite NaX.

TG/DSC curves of nano-NaX and micro-NaX are shown in figure 20. The endothermic peaks in DSC curve of micro-NaX at 120°C can be attributed to the removal of physical adsorbed water on the surface of the materials and that at 332°C is because of the removal of chemical adsorbed water in the pores. The total weight loss determined by TG curve is about 18.3%. The exothermic peak at 869°C without weight loss might be assigned to the phase transformation and micro-NaX.

Two similar endothermic peaks at 102 and 345°C and an exothermic peak at 789°C are observed in DSC curve of nano-NaX. The total weight loss of nano-NaX is higher than that of micro-NaX (24.1% compared to 18.3%) due to the porosity of nano-NaX being higher than that of micro-NaX.

\( \mathrm{N}_2 \) adsorption/desorption isotherms at 77 K and pore size distribution of nano-NaX and micro-NaX are shown in figure 21. The isotherm of micro-NaX is type I (defined by IUPAC) [9] which is the characteristic of microporous material. However, the loop started at \( p/p_0 \approx 0.45 \) can be observed in the isotherm of nano-NaX, which belongs to type II [9] because of the condensation of nitrogen in mesopores of the materials. These mesopores could be formed between the nanometer crystals.

Pore distribution analyzed following the method in [10] are shown in figure 22. The average pore sizes of both micro- and nano-NaX are 0.81 nm. However, small pore distribution in ~10.8 nm region can be observed in nano-NaX, it might be the secondary porous system formed between the nanometer crystal and causes the loop in the isotherm as mentioned above.

The BET surface areas of nano-NaX and micro-NaX are 573 and 520 m\(^2\) g\(^{-1}\) respectively. The external surface of nano-NaX is 92 m\(^2\) g\(^{-1}\) and that of micro-NaX is 39 m\(^2\) g\(^{-1}\). The increase of the external surface is due to the reduction of

Table 5. Crystal size of zeolite NaX calculated by Scherrer equation.

| Sample    | H\(_2\)O/Al\(_2\)O\(_3\) ratio in gel | FWHM  | 2\( \theta \)(°) | Crystal size (nm) |
|-----------|--------------------------------------|-------|-----------------|------------------|
| X96-12-70H | 70                                   | 0.487 | 6.036           | 23               |
| X96-12-90H | 90                                   | 0.350 | 6.038           | 42               |
| X96-12-110H| 110                                  | 0.285 | 6.048           | 158              |
| X96-12-130H| 130                                  | 0.281 | 6.052           | 352              |

Figure 11. XRD patterns of X00-12 (a), X24-12 (b), X48-12 (c), X72-12 (d), X96-12 (e), X120-12 (f) and X144-12 (g).
crystal sizes (table 8). The data in table 8 show the outstanding characteristics of nano-NaX compared to those of micro-NaX that can affect the adsorption ability of nano-NaX.

3.8. Dynamic cumene adsorption on nano-NaX and micro-NaX.

Figure 23 shows the cumene adsorption capacity of nano-NaX and micro-NaX. Both samples adsorb cumene vapor well. However, the adsorption capacity of nano-NaX is better. During the first 15 min, nano-NaX adsorbs nearly 90% cumene vapor in the flow; the cumene content in the outlet is less than 800 ppm.

The breakthrough curve obtained with nano-NaX is steeper than that obtained with micro-NaX. The steeper the breakthrough curve, the higher this adsorption rate constant. This is likely due to the smaller particle size of nano-NaX.
### Table 6. Influence of ageing time to the crystallinity and crystal size of nanozeolit NaX.

| No. | Sample code | Ageing time (h)– crystallized time (h) | Crystallinity by XRD(%) | Average crystal size, nm |
|-----|-------------|--------------------------------------|-------------------------|-------------------------|
|     |             |                                       | By XRD                  | By TEM                  | By SEM                  |
| 1   | X00-12      | 00–12                                 | 60                      | 60                      | 70                      | 157                     |
| 2   | X24-12      | 24–12                                 | 75                      | 56                      | 65                      | 155                     |
| 3   | X48-12      | 48–12                                 | 80                      | 56                      | 65                      | 140                     |
| 4   | X72-12      | 72–12                                 | 82                      | 45                      | 50                      | 92                      |
| 5   | X96-12      | 96–12                                 | 92                      | 25                      | 32                      | 54                      |
| 6   | X120-12     | 120–12                                | 90                      | 44                      | 50                      | 95                      |
| 7   | X144-12     | 144–12                                | 88                      | 43                      | 50                      | 98                      |

**Figure 14.** XRD patterns of X96-06 (a), X96-12 (b), X96-18 (c), X96-24 (d), X96-48 (e), X96-72 (f) and X96-96 (g).

### Table 7. Influence of crystallizing time.

| No. | Sample code | Ageing time (h)– crystallized time (h) | Crystallinity by XRD(%) | Average crystal size, nm |
|-----|-------------|--------------------------------------|-------------------------|-------------------------|
|     |             |                                       | By XRD                  | By TEM                  | By SEM                  |
| 1   | X96-06      | 96-06                                 | 55                      | 30                      | 35                      | 70                      |
| 2   | X96-12      | 96-12                                 | 92                      | 25                      | 32                      | 54                      |
| 3   | X96-18      | 96-18                                 | 90                      | 38                      | 40                      | 65                      |
| 4   | X96-24      | 96-24                                 | 90                      | 42                      | 52                      | 68                      |
| 5   | X96-48      | 96-48                                 | 88                      | 42                      | 55                      | 91                      |
| 6   | X96-72      | 96-72                                 | 85                      | 50                      | 61                      | 97                      |
| 7   | X96-96      | 96-96                                 | 84                      | 50                      | 62                      | 105                     |

### Table 8. Characteristics of nano-NaX and micro-NaX.

| Sample | BET surface area (m² g⁻¹) | External surface area (m² g⁻¹) | Pore Distribution (nm) | Crystal size (nm) | Total pore Volume (cm³ g⁻¹) | Micropore Volume (cm³ g⁻¹) |
|--------|---------------------------|-------------------------------|------------------------|------------------|----------------------------|---------------------------|
|        |                           |                               |                        | By XRD           | By SEM                     | By TEM                    |
| Nano-NaX | 573                      | 92                            | 0.81; 10.8             | 25               | 54                        | 32                        | 0.350                     | 0.159                     |
| Micro-NaX | 520                      | 39                            | 0.81                   | 400              | 420                       | –                         | 0.322                     | 0.223                     |

(25 nm by XRD instead of 400 nm for micro-NaX). The breakthrough time is shorter for nano-NaX (35 min) than for micro-NaX (40 min).

Nano-NaX has smaller crystal size, higher external surface area and higher pore volume (table 8), so the adsorption capacity is higher. Moreover, nano-NaX has
Figure 15. SEM images of X96-06 (a), X96-12 (b), X96-18 (c), X96-24 (d), X96-48 (e), X96-72 (f) and X96-96 (g).

Figure 16. TEM images of X96-06 (a), X96-12 (b), X96-18 (c), X96-24 (d), X96-48 (e), X96-72 (f) and X96-96 (g).
secondary porous system which is much larger than the diameter of cumene, so it can adsorb cumene vapour easily leading to the fast decrease of cumene concentration in the outlet.

When the secondary porous system is filled up with cumene vapor, the adsorption will take place in the micropores. The increase of crystal size of micro-NaX makes both the external and internal transport of the adsorbate more difficult [11].
After each adsorption round, the adsorbent was desorbed and then used again. The adsorption capacity of nano-NaX after 6th round adsorption is shown in figure 24. The breakthrough curve after the 6th round is the same as that after the 1st round. This means that synthesized nano-NaX is very stable and has high adsorption capacity.

4. Conclusions

Nanozeolite NaX has been successfully synthesized from Vietnamese kaolin. The material has surface area of 573 m$^2$ g$^{-1}$, external surface area of 92 m$^2$ g$^{-1}$, pore distribution at 0.81 and 10.8 nm; crystallinity of 92%, crystal size of 25 nm and thermal stability up to 789 $^\circ$C.

Influence of crystallizing temperature, Na$_2$O/Al$_2$O$_3$, SiO$_2$/Al$_2$O$_3$, H$_2$O/Al$_2$O$_3$ molar ratio in gel, ageing time and crystallizing time on the synthesis of nanozeolite NaX have been investigated. The optimal synthesis conditions are: molar ratio in gel of mol 5Na$_2$O.Al$_2$O$_3$.4SiO$_2$.70H$_2$O.1.2EDTA.2NaCl, ageing in 96 h with mixing and crystallizing at 80 $^\circ$C.

Nanozeolite NaX has higher adsorption capacity for cumene than conventional micrometer zeolite NaX. The adsorption stability of nanozeolite NaX is very good.

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