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*Article*

## Facile Hydrothermal Synthesis of Zeolitic ANA Membrane from Raw Kaolin

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**Abstract.** The present paper reported a preparation of zeolitic ANA (analcime) membrane on porous ceramic support by in situ synthesis method using raw kaolin as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> source with the molar composition of Al<sub>2</sub>O<sub>3</sub> · 2.3SiO<sub>2</sub> · 3.6Na<sub>2</sub>O · 140.4H<sub>2</sub>O at hydrothermal temperature 200 °C. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to characterize the ANA membrane. The effects of aging time and hydrothermal time on the synthesis were investigated. The porous ceramic supports were prepared by adding 10.0 wt% of cristobalite and varying an amount of pore formers (activated carbon and calcite) by sintering at 1400 °C. This resulted in the high crystallinity of ANA observed on the support which was prepared from mixing of 2.5 wt% of activated carbon and 2.5 wt% of calcite. In addition to aging, it was observable that small crystals seemed to spread completely on the support within 3 days of aging. It seems that the longer the hydrothermal time is, the more obvious the crystals tightly bound with the support becomes.

**Keywords:** ANA membrane, porous ceramic support, raw kaolin, pore former, mullite.

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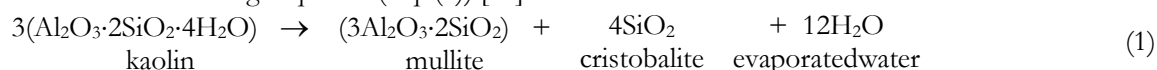
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## 1. Introduction

Recently, the field of zeolite membranes significantly attracts various kinds of applications [1] in gas or liquid separations [2, 3], membrane reactors [4, 5] and sensors [6, 7] not only because of its selective absorption, uniform but also its molecular size pore. More importantly, zeolite membrane also has high mechanical strength, thermal and chemical stability compared to organic membranes. The hydrophilic zeolite membranes such as NaA zeolite [8–14], faujasite-type zeolite (X and Y) [15], and mordenite [16] membrane have been widely applied to break the azeotrope of ethanol and water for preparation anhydrous ethanol, especially NaA zeolite membrane. ANA zeolite should be one alternative for those applications because the aperture of the 8-ring pore opening is  $1.6 \times 4.2 \text{ \AA}$ . Therefore small pore size of ANA makes the separation of small molecules by difference in size possible. Thus, small water molecules as about  $2.6 \text{ \AA}$  are expected to be separated from bigger molecule of ethanol as  $4.4 \text{ \AA}$ . The synthesis of ANA with natural raw materials such as diatomite [17], perlite [18, 19] and kaolin [20, 21] is more economically advantageous than the synthesis with chemicals because of its cost effectiveness.

To make the best use of the synthesis of ANA, there are several methods to synthesize zeolite membrane. However, the two common ones are in situ crystallization method and the secondary-growth method. These methods used a pure chemical of sodium aluminosilicate gel in alkaline solution whose crystal growth was on the supports of  $\alpha$ - or  $\gamma$ -alumina and mullite [22, 23]. More interestingly, mullite is a ceramic support gaining more popularity with its more advantages. That is it has a high melting point, superior high temperature strength, exceptional thermal shock resistance, oxidation resistance, high electrical resistivity and good chemical stability in harsh chemical environments [24, 25]. It also can be produced from sintering process of fly ash and bauxite [25]. Moreover, mullite based ceramics can be simply obtained by calcination of kaolin [26]. Consequently, the transformation of kaolin into mullite can be observed at a high temperature in this following sequence (Eq. (1)) [27]:



Generally, porous mullite-based ceramics can be produced by various techniques. The most common one is by using agents as pore former such as graphite [28], Al and Mg metallic powders [29] and calcite ( $\text{CaCO}_3$ ) [30] to control or help in forming pores with suitable distribution and sizes. Furthermore, another technique to produce porous mullite is through the removal of cristobalite produced from calcined bodies of sintered kaolin by leaching with strong alkali solutions [31, 32].

Until now, there are only few studies focusing on how to prepare zeolite layer from solid phase like kaolin on mullite support. What has been publicly reported is just the synthesis of hydroxysodalite (H-SOD) from metakaolin on porous mullite tubular support [31]. Thus, this gives rise to this present research whose aim focuses on simple preparation of high crystalline hydrophilic ANA membrane with raw kaolin which is one of the cheapest and most abundantly available silica and alumina source in our country, Thailand, for water/ethanol separation in a future towards separation/pervaporation performance.

## 2. Experiment

### 2.1. Materials

Raw kaolin obtained from Narathiwat province (Thailand) was used as starting material for synthesis of ANA in order to prepare porous ceramic supports. Firstly, it was sieved with  $63 \mu\text{m}$  mesh before being used in the later steps. The chemical composition in weight percent of raw kaolin were 40.9% $\text{SiO}_2$ , 30.7% $\text{Al}_2\text{O}_3$ , 3.6% $\text{Fe}_2\text{O}_3$ , 4.3% $\text{Na}_2\text{O}$ , 4.3% $\text{K}_2\text{O}$ , 2.7% $\text{MgO}$ , 0.3% $\text{CaO}$ , 0.3% $\text{MnO}_2$ , 0.1% $\text{TiO}_2$  and 12.6%LOI. In this process, cristobalite prepared from rice husk and hydrochloric acid (Merck), as well as pellets of sodium hydroxide (Merck) were used in the synthesis of ANA. Activated carbon and calcite were purchased from Panreac and QR $\ddot{e}$ C, respectively.

## 2.2. Preparation of Porous Ceramic Supports

### 2.2.1. Preparation of cristobalite

Cristobalite, one of the ingredients is needed for making the ceramic discs as it helps to maintain a thermal expansion coefficient of ceramic plate to be constant [33]. These following steps were taken to prepare cristobalite from rice husk. Firstly, rice husk (10.0 g) was washed with tap water followed by deionized water (DI) and dried at 110 °C. Then it was reacted with 100.0 mL of 1 M HCl solution and boiled for 3 hours. Later, the obtained solid was washed with DI water until pH was 7 and dried at 110 °C. After that it was calcined at 700 °C for 4 hours to eliminate organic compound [34]. After white powders of pure silica were obtained, then, silica was sieved with 63 µm mesh and followed by calcined at 1400 °C to transform silica into cristobalite [35].

### 2.2.2. Preparation of porous ceramic discs

The followings are the ingredients for preparing the porous ceramic discs i.e. 10.0 wt% of cristobalite, 2.5 wt% and 5.0 wt% of activated carbon and/or calcite (CaCO<sub>3</sub>) as pore former and 85.0-87.5 wt% of kaolin. Generally, to start with, DI water was added into the ingredient followed by sonication for 60 min, and then it was heated, stirred and evaporated until the mixtures became slurry. When the slurry was dried in an oven at 110 °C, 13.0 g of the obtained sample was later ground and compressed as a disc (5.5 cm diameter×0.5 cm thick) about 1000 psi by uniaxial dry pressing. Next, the disc was put on crucible and sintered at 1400 °C in the furnace for 90 min with a heating and cooling rate of 2.0 °C/min to burn off the organic or inorganic to transform the mixture into porous ceramic supports. Then the porous ceramic supports was cleaned with DI water and dried at 110 °C. All the supports were carried out by using gloves. The percent of shrinkage of all the prepared supports were about 24%.

Normally, the apparent porosity were conducted by analytical balance and Archimedes' method [36]. The porous ceramic supports were prepared from pore former of 2.5 and 5.0 wt% of activated carbon and 2.5 and 5.0 wt% of calcite denoted as 2.5A and 5A and 2.5Ca and 5Ca, respectively. Similarly, the porous ceramic support from the mixture of pore former of 2.5 wt% activated carbon and 2.5 wt% calcite was denoted as 2.5ACa.

## 2.3. ANA Membrane Synthesis

To begin with, the mixture of raw kaolin (2.0 g) and 2.50 M NaOH (16.2 mL) was stirred for 1 hour, and then it was transferred into a stainless steel autoclave followed by immersing porous ceramic supports into the mixture with the condition of no aging and with aging of 1, 2 and 3 days at an ambient temperature. After that, autoclave was placed in an oven at 200 °C with the reaction time of 12, 18 and 24 hours. Then the autoclave was cooled down to room temperature. Finally, the products were washed with DI water until pH 7 and dried at 110 °C.

## 2.4. Characterization

The chemical composition of raw kaolin obtained from energy dispersive X-ray fluorescence (EDXRF) analysis using a Model XGT-5200 of Horiba, with X-ray tube of rhodium anode. The X-ray diffraction (XRD) patterns were collected using a Bruker D2 Phaser with Cu-K $\alpha$  radiation (40 kV and 40 mA). Data collection was carried out in the 2 $\theta$  rang 10-45° at step size of 0.02°. Micrographs of scanning electron microscope (SEM) different samples were performed with JSM-6010LV model (JEOL) operating with an accelerating voltage of 20 kV.

## 3. Results and Discussion

### 3.1. Porous Ceramic Supports

The XRD patterns of raw kaolin, calcined kaolin and the prepared porous ceramic supports were shown in Fig. 1. While Fig. 1(g) shows the main diffraction peak of kaolin and impurity phase of quartz. Figure 1(a) demonstrates a sharp peak of silica phase of cristobalite and mullite phase after calcination of raw kaolin at

1400 °C. Figures 1(b)–(f) indicates no existence of an impurity phase of quartz in all the porous ceramic supports except the sample of 5A and 2.5ACa. Figures 1(d)–(e) also represents an noticeable a phase of anorthite in the sample of 2.5Ca with the increased amount of calcite to 5.0 wt%. In Fig. 1(e), resulting in an appearance of additional phase of wollastonite. However, Fig. 1(f), 2.5ACa sample showed the peaks of both wollastonite and anorthite with much more obviously increasing intensity peaks of anorthite.

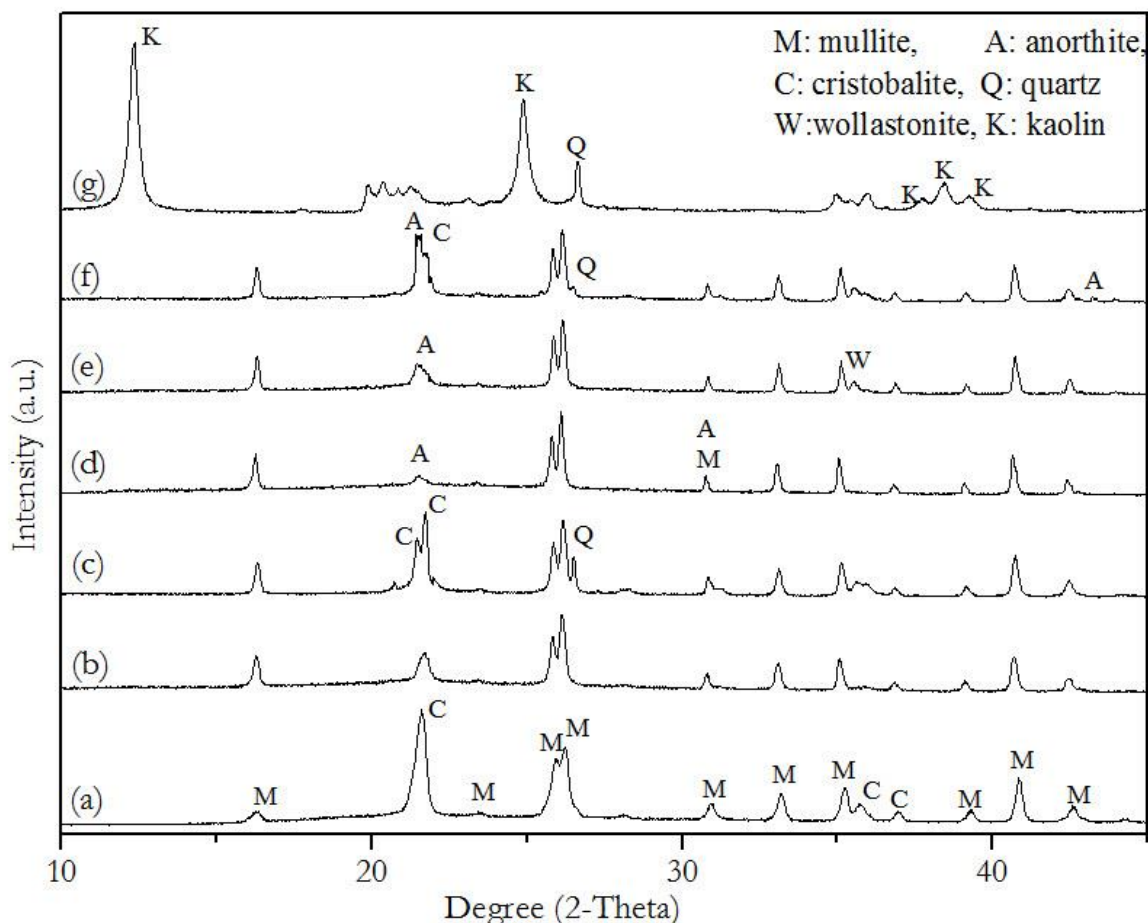


Fig. 1. XRD patterns of porous ceramic supports: (a) calcined kaolin, (b) 2.5A, (c) 5A, (d) 2.5Ca, (e) 5Ca, (f) 2.5ACa and (g) raw kaolin.

Figure 2 shows the surface and cross-section of 2.5A and 2.5Ca by SEM micrographs. This indicates that when the calcination of  $\text{CaCO}_3$  at high temperature regime corresponds to decomposition of  $\text{CaCO}_3$  into  $\text{CaO}$  and released  $\text{CO}_2$  gas, then  $\text{CO}_2$  gas creates the porous texture [30, 37]. Likewise, the sample of 2.5A showed both spherical and elongated pores became bigger within the range 20–40  $\mu\text{m}$  than those of 2.5Ca (10–30  $\mu\text{m}$ ). The cross-sections of both 2.5A and 2.5Ca showed clearly distribution of the pores into the body.

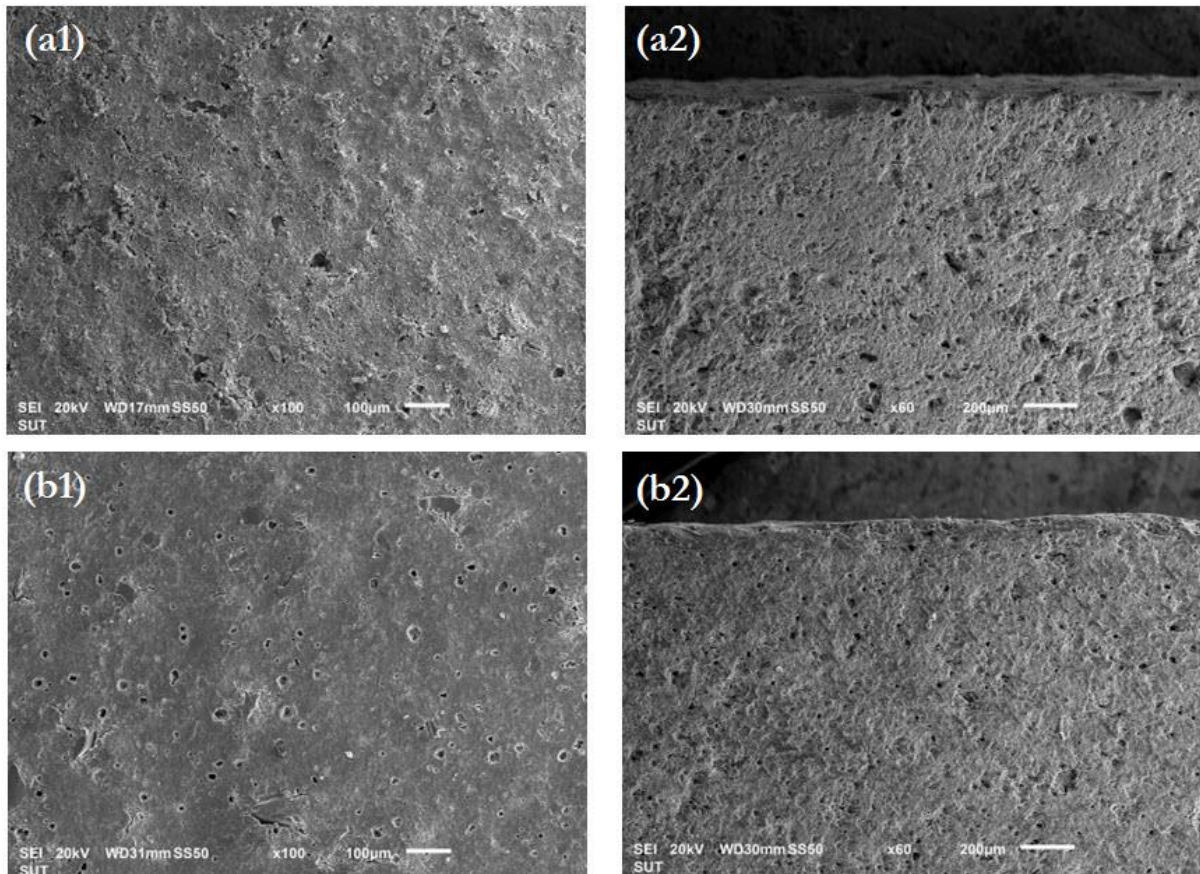


Fig. 2. Top view and cross-sectional SEM micrographs of the 2.5A ((a1) and (a2)) and 2.5Ca ((b1) and (b2)).

Figure 3 demonstrates SEM micrographs of surface and cross-section of 5A, 5Ca and 2.5ACa. The sample of 5A showed the pore sizes were larger than those of 5Ca and 2.5ACa with the pore size within the range of 60-80  $\mu\text{m}$ , 20-60  $\mu\text{m}$  and 20-50  $\mu\text{m}$ , respectively. The cross-sections of these samples showed a higher pore density than that of 2.5A and 2.5Ca and the pores spread through the body. The pore size and the porosity of all the porous ceramic supports are summarized in Table 1.



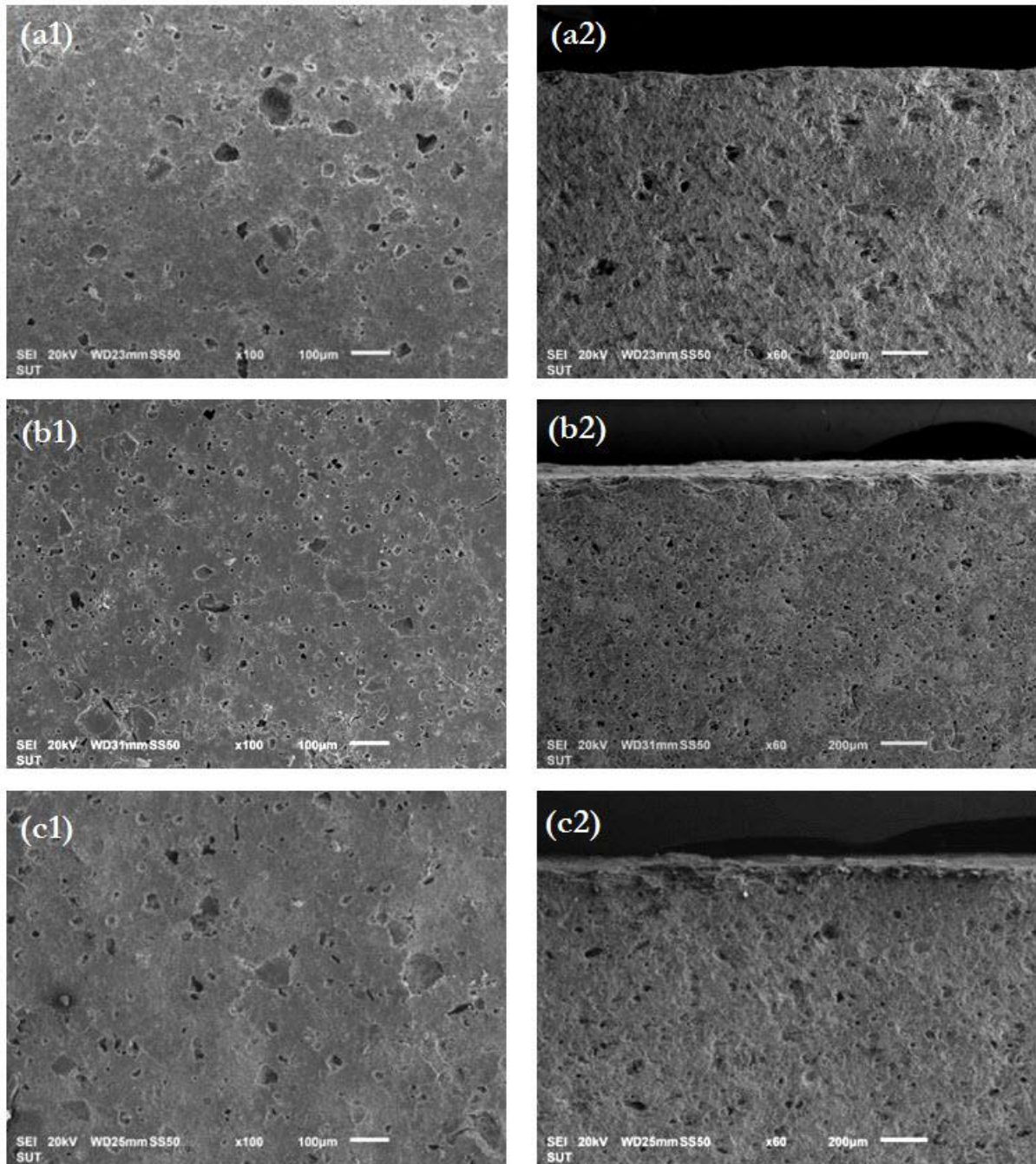


Fig. 3. Top view and cross-sectional SEM micrographs of the 5A ((a1) and (a2)), 5Ca ((b1) and (b2)) and 2.5ACa ((c1) and (c2)).

Table 1. The average pore size and percentage of porosity of porous ceramic supports.

Porous ceramic supports	2.5A	2.5Ca	2.5ACa	5A	5Ca
The range pore size (µm)	20-40	10-30	20-50	60-80	20-60
Porosity (%)	14.6	10.0	22.6	26.3	23.9

### 3.2. Characteristics of ANA Membrane

#### 3.2.1. Effects of porous ceramic supports

The XRD patterns in Fig. 4(a)–(c) show only a single phase of ANA on 2.5A, 2.5Ca and 2.5ACa, but the sharpest peak of XRD with the highest intensity of ANA was observed in 2.5ACa indicating that a crystal is perfect with more amounts of ANA crystals. These results are consistent with those of SEM (see Fig. 5 and 6). The appearance of mixed phase of ANA and cristobalite on 5A and 5Ca (Fig. 4(d)–(e)) may be due to the better leaching of silica with NaOH solution resulting in larger porous ceramic and higher porosity like 5A and 5Ca.

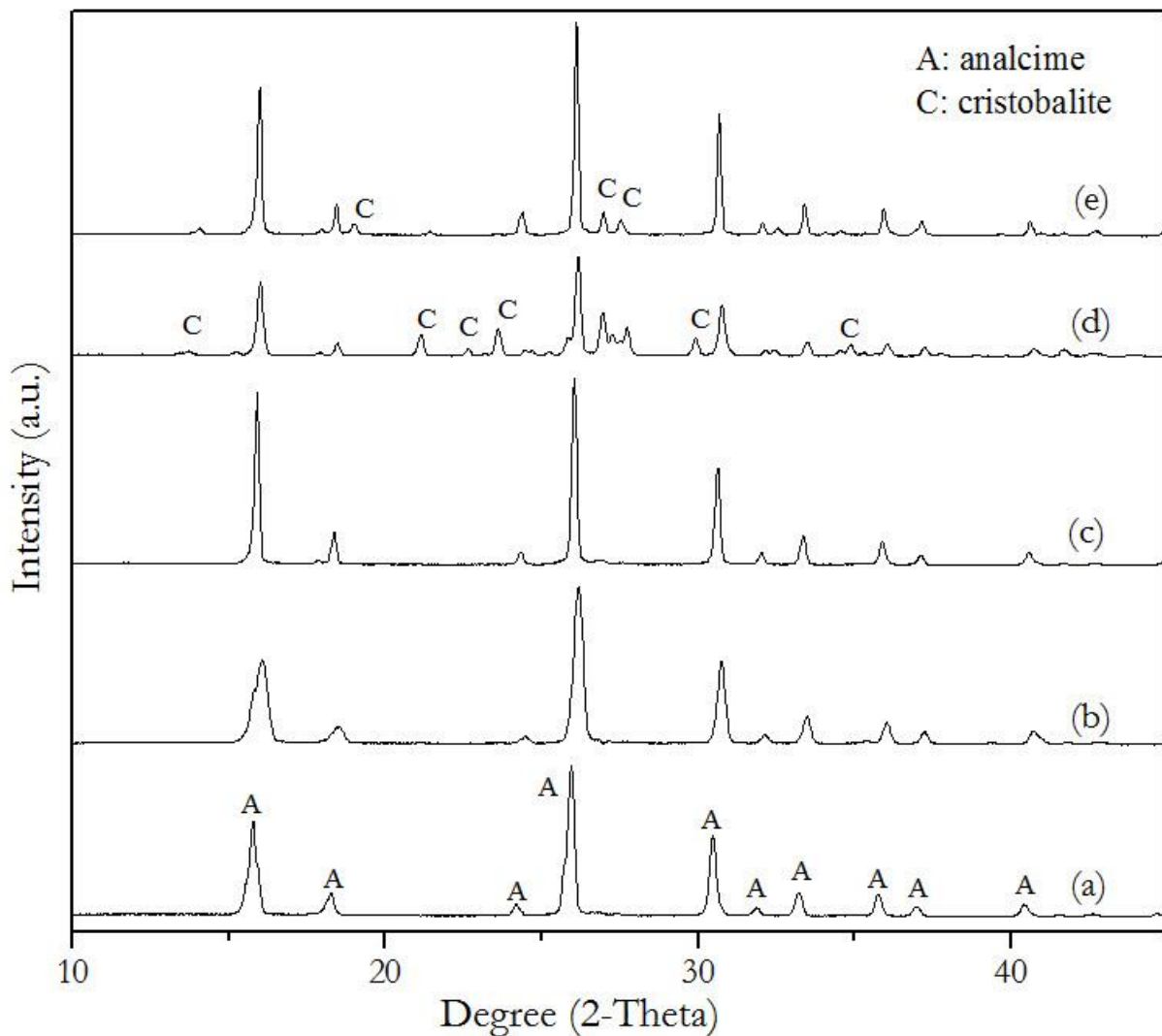


Fig. 4. XRD patterns of ANA membrane on (a) 2.5A, (b) 2.5Ca, (c) 2.5ACa, (d) 5A and (e) 5Ca for 24 hours.

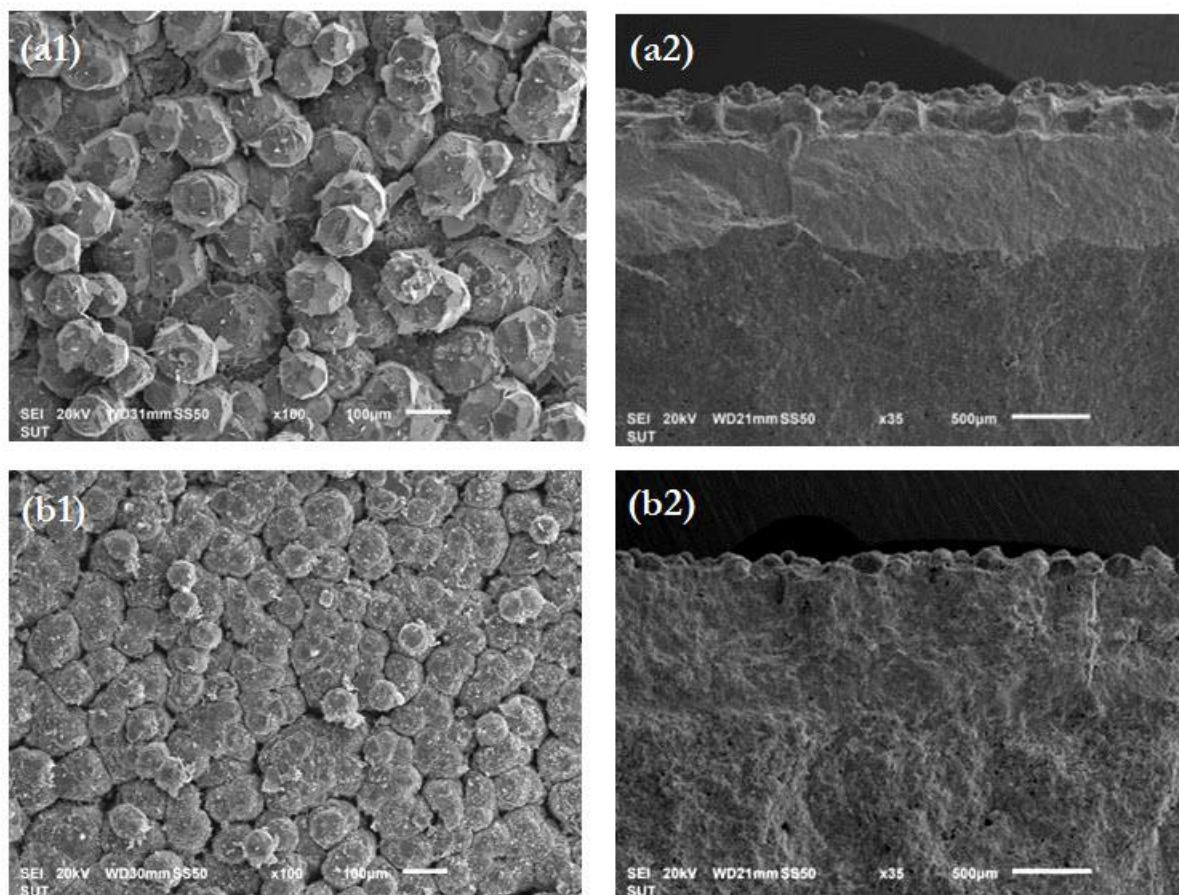


Fig. 5. Surface and cross-sectional SEM micrographs of the ANA membrane on 2.5A ((a1) and (a2)) and 2.5Ca ((b1) and (b2)) for 24 hours.

Figure 5 shows SEM micrographs of ANA membrane on 2.5A and 2.5Ca. The surface of 2.5A was covered by continuously and increasingly growing ANA crystals while the surface of 2.5Ca obviously showed the space between ANA crystals. The cross-section of the porous ceramic disc demonstrates the crystal layers of both 2.5A and 2.5Ca bound with the disc. Figure 6 illustrates SEM micrographs of ANA crystals covering on 2.5ACa, 5A and 5Ca. ANA crystals completely cover on the surface of 2.5ACa over 5A and 5Ca which are partially covered by ANA crystals, corresponding to the results of XRD (Fig. 4(c)–(e)). The cross-section of ceramic disc of 5A indicates a horizontal crevice from the top plate about 500  $\mu\text{m}$  but it was not observed in 5Ca and 2.5Aca. It may be the result of 5A containing higher porosity and larger pore size compared to the other supports (see Table 1). However, these supports contained ANA layer bound with the ceramic disc. It can be concluded from all of the results that 2.5ACa is suitable as porous ceramic support for in situ synthesis method with the raw kaolin in order to prepare ANA membrane.



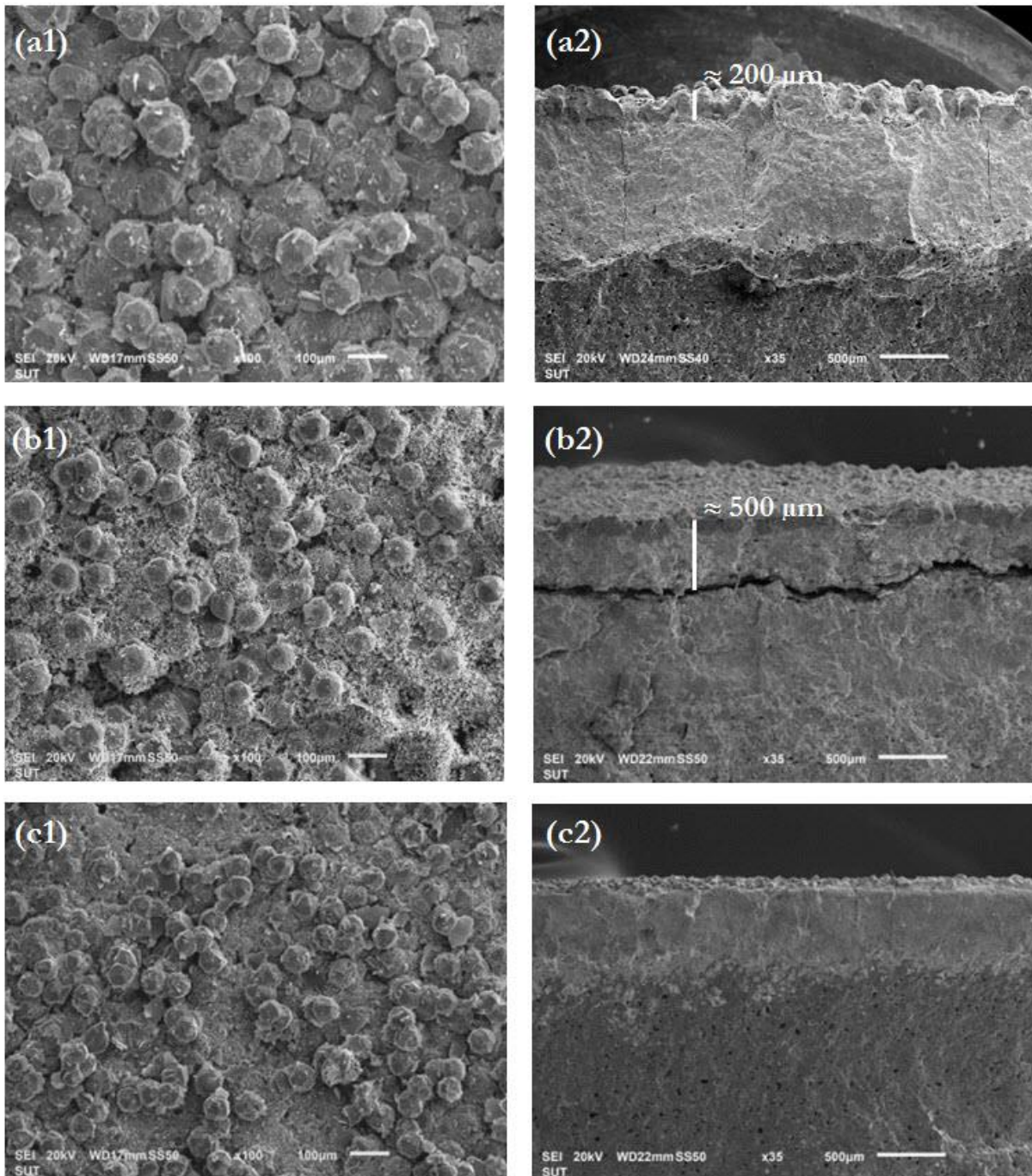


Fig. 6. Surface and cross-sectional SEM micrographs of the ANA membrane on 2.5ACa ((a1) and (a2)), 5A ((b1) and (b2)) and 5Ca ((c1) and (c2)) for 24 hours.

### 3.2.2. Effects of hydrothermal time

SEM micrographs of the synthesized ANA on 2.5ACa at different hydrothermal times of 18 and 24 hours were shown in Figs. 7(a1) and 6(a1), respectively. They indicate that the longer hydrothermal time was, the bigger the crystal size became. This was consistent with the elsewhere report [38]. The sizes of crystals were about 40-84  $\mu\text{m}$  and 112-152  $\mu\text{m}$  for hydrothermal time of 18 and 24 hours, respectively. However, ANA membrane could not be synthesized with hydrothermal time of 12 hours due to the occurrence of peeling of ANA layer out of the ceramic disc.

Figure 7(a2) illustrates SEM micrographs of the cross-sections of ANA membrane with 18 hours of hydrothermal time. The thickness of the ANA layer is about 220  $\mu\text{m}$ . This includes a layer between ANA

layer and the disc which looks like its seam. If the hydrothermal time is extended to 24 hours (Fig. 6(a2)), the internal growth of crystals was allowed to be sufficiently done. This caused the crystals to bind with the disc resulting in layer thickness about 200  $\mu\text{m}$ . This might be influenced by the increased amount of the elution of the support to alkaline solution causing the intermediate layer to be packed densely with zeolite and mullite [12].

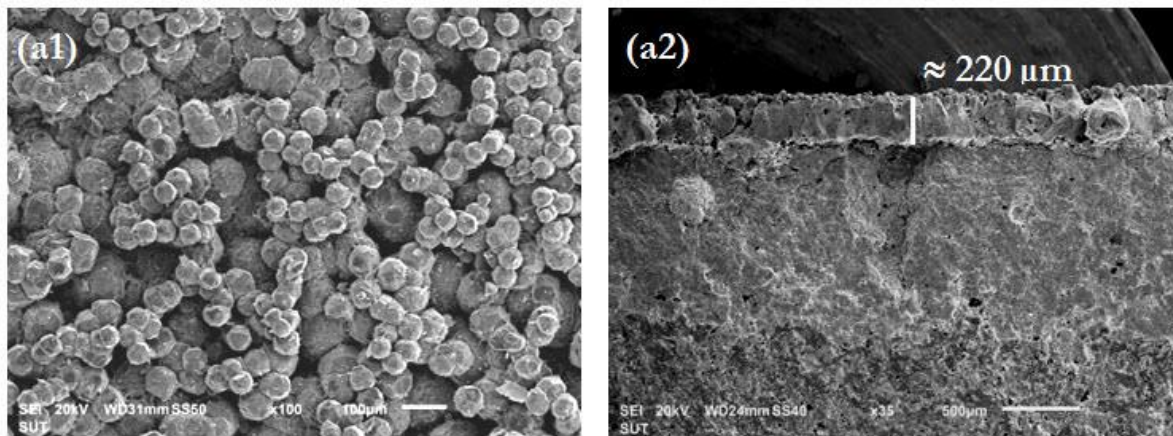


Fig. 7. Surface (a1) and cross-sectional (a2) SEM micrographs of the ANA membrane on 2.5ACa for 18 hours.

### 3.2.3. Effects of aging

Figure 8 shows that SEM micrographs of ANA membrane with the effect of aging varied from 1 day to 3 days. The average crystal size is about 25–37  $\mu\text{m}$ . It is noticeable that the size of ANA crystals is within the range of pore size of 2.5ACa (20–50  $\mu\text{m}$ ). The comparison of the crystal size in the ANA membrane synthesis with and without aging indicates that the smaller size of the crystal was obtained with aging while a larger size occurred without aging (Fig. 7(a1)).

This may result from increasing number of nuclei or nuclei precursors in the synthesis with aging resulting in the smaller zeolite crystals and an increase in the amount of zeolite [39, 40]. The small crystal size and a number of zeolite crystals increase instruct the number and the size of the gaps in the membrane reduce. The small crystal zeolite membrane were proposed to form multi-layers compared with large crystal zeolite membrane, the layer of crystal can close gaps and cracks of the preceding layer [40]. Possibility, the diffusion of polar group as water molecules enhance with smaller crystal size and number of crystals. The thin cross-section of ANA layer (Fig. 8(a2)) is about 50  $\mu\text{m}$  compared to that about 220  $\mu\text{m}$  without aging. The decreasing of zeolite thickness affect to the increasing of water flux of the pervaporation system due to rapid diffusion of water molecules from the retentate side to the permeate side [11, 41, 42].

The XRD patterns of 1 day and 2 days of aging (Fig. 9(a)–(b)) exhibit both the sharp peaks of ANA phase and the small broad peak of mullite at 23.7°. Nevertheless, the broad peak disappeared with 3 days aging indicating that the occurring crystals overspread completely on the surface of the support. The coverage of ANA crystals through the disc presented quality in terms of maximum surface coverage, interlocked crystal arrangement and rendering better separation factor for water/ethanol mixture [14]. Therefore, ANA membranes prepared with aging is effective increasingly for separation of water from ethanol.



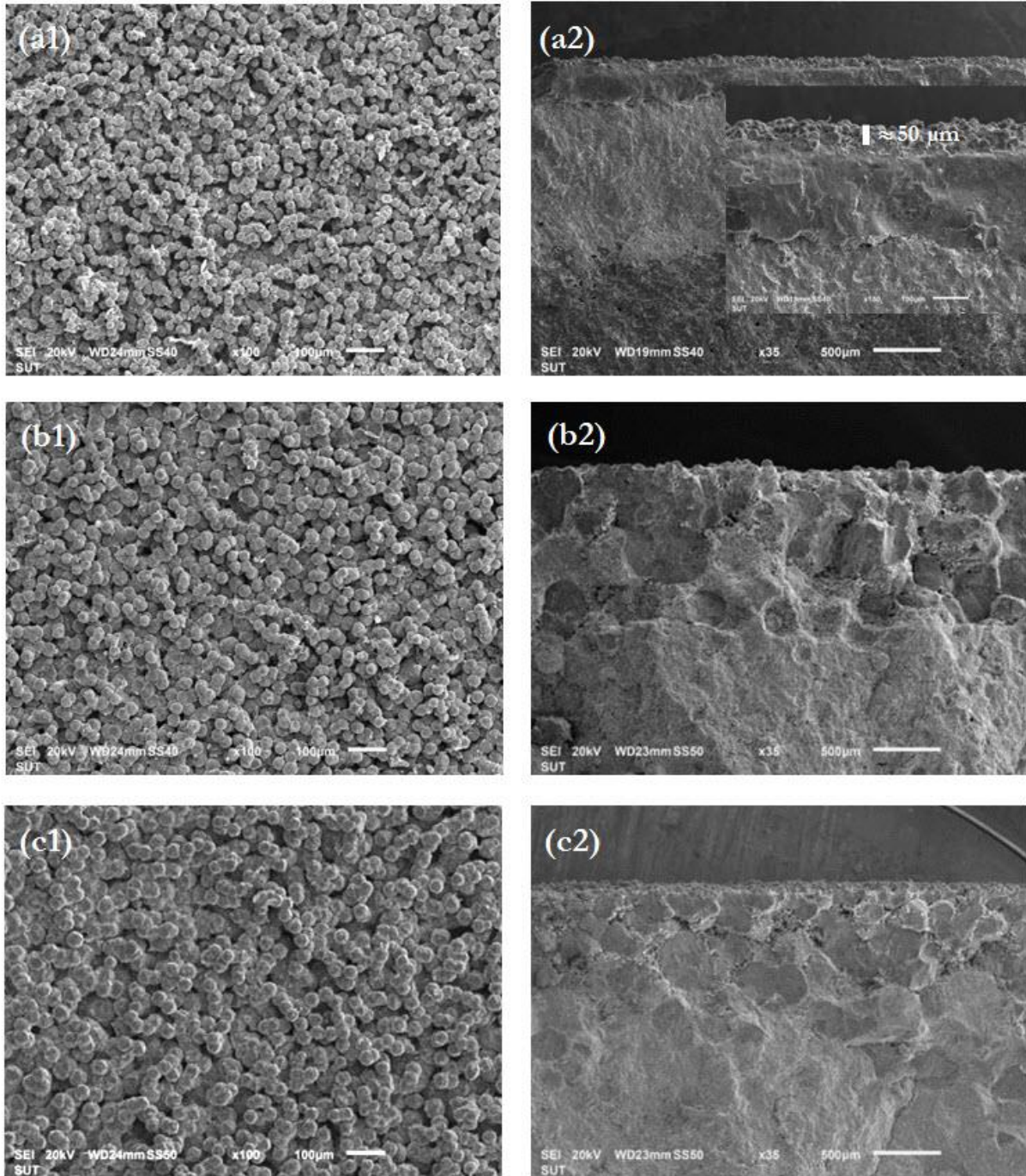


Fig. 8. Surface and cross-sectional SEM micrographs of the ANA membrane for aging 1 day ((a1) and (a2)), 2 days ((b1) and (b2)) and 3 days ((c1) and (c2)) on 2.5ACa for 18 hours.

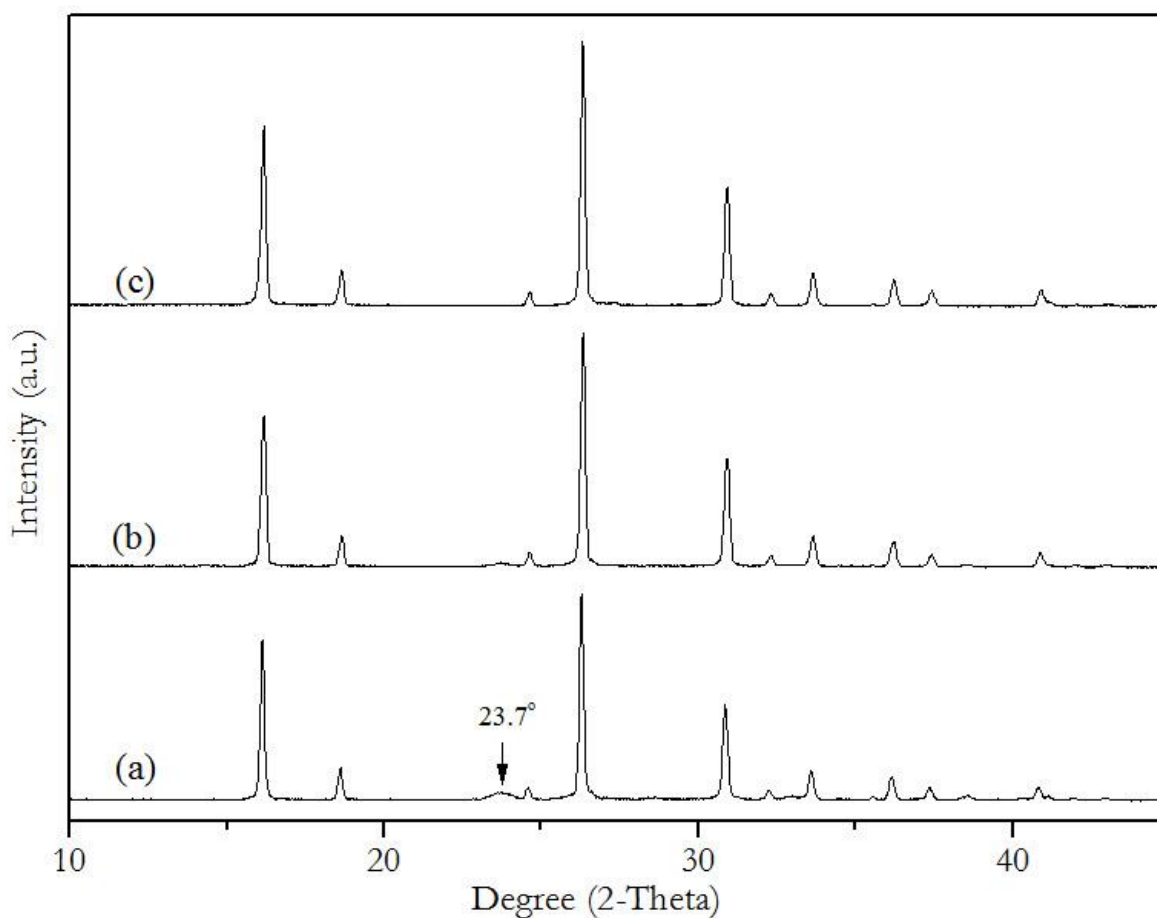


Fig. 9. XRD patterns of the ANA membrane for aging (a) 1 day, (b) 2 days and (c) 3 days on 2.5ACa for 18 hours.

#### 4. Conclusions

The findings from this study prove that high crystalline ANA membranes were successfully synthesized from raw kaolin as starting material. The type and the amount of pore formers (activated carbon and calcite) affect the average pore size, percent porosity and component of the support. Moreover, it plays a significant role on the dissolution of cristobalite from the support. The most suitable ceramic support found in this work was prepared from the ingredient of 10.0 wt% cristobalite, 2.5 wt% activated carbon and 2.5 wt% calcite and 85.0 wt% raw kaolin and ANA membrane with small well crystals, lots of number of crystals and thin layer of the ANA membrane was obtained from synthesis with aging. These characteristics are required for the membrane with good quality for water/ethanol separation.

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