

Study the Effect of Seeding Suspension Concentration of DD3R Particles on the Modified Surface of α -Alumina Support for Preparing DD3R Zeolite Membrane with High Quality

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Abstract

In this study, seeding of DD3R particles as an important step in the synthesis of DD3R membrane with secondary growth method was investigated. Dip-coating method is used for seeding of DD3R particles on the modified surface of α -alumina supports. 0.1, 0.2 and 0.3 wt% aqueous suspensions of the DD3R seeds were prepared and each support was coated three times with dipping time of 240 s. Scanning electron microscopy (SEM) analysis was used for the investigation of the quality of seed layer formed on the support. It is shown that the uniform layer of seeds was formed with 0.2 wt% seed suspension concentration. DD3R zeolite membrane was synthesized via hydrothermal method on the support seeded with 0.2 wt% seed suspension concentration. The X-ray diffraction and SEM analysis confirmed the synthesis of uniform DD3R zeolite membrane layer on the support which can be due to the uniform distribution of the DD3R seeds. Single gas permeation tests of N₂, CO₂ and CH₄ were carried out, so that good perm-selectivity for gas mixtures was observed.

Keywords:

Seeding;
Seed Suspension Concentration;
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1- Introduction

Natural gas purification (from CO₂ and N₂) is so important for using the CH₄ as feed or a fuel. But, conventional approaches for separation of CO₂ and N₂ are expensive units especially at high pressures of natural gas wells [1]. So, Membrane separation by low energy costs and continuous operation can be applied in natural gas processes for separation and purification [2]. Among the membranes, zeolite membranes with well-defined nano-pores have expanded the effort in preparing a membrane with high selectivity and permeance for separation purpose [3, 4]. DD3R zeolite membrane as a new type of zeolite membrane have attractive potential for effective separations of CO₂ and N₂ from CH₄ due to its pore channel of 0.36 nm × 0.44 nm [5]. But in spite of this potential in separation of gases with small molecules, few studies have been done on the synthesis of DD3R zeolite membrane. Because synthesis process of this type of membrane is hurdle and take long time [6]. Therefore, using secondary growth method as a vital technique for accelerating the synthesis of DD3R zeolite membrane with high quality is needed [7, 8]. Effective seeding is one of the essential step to obtain thin and defect free zeolite membranes that prepared with secondary growth method on mesoporous tubular supports. DD3R zeolite membrane was first synthesized by Tomita et al. [9] on macro porous alumina support and reported good separation performance in natural gas purification [9]. Then, some other researchers studied the synthesis of DD3R membrane. But, they reported a poor performance with low quality of membrane layer. According to the literature, the most DD3R membranes with good performance were fabricated by Tomita et al., Himeno et al. and their co-workers at NGK insulator [5, 10].

Because of the mentioned importance of seeding, the effective investigation of the different parameter of seeding is necessary [7]. Literature result indicated that the effect of different parameter of seeding was investigated just by Yajima et al. [11]. They studied a seed crystal conditions such as seed crystal average particle diameter and seed crystal weight

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per unit area and optimized the values for each parameter. By using these optimized parameters, a uniform membrane layer with low thickness and high permeability was obtained. As the best of our knowledge, the concentration of seeding solution was one of the important parameters in DD3R zeolite membranes synthesis where nobody has yet reviewed.

In the present paper, the α -alumina supports modified by TiO₂-bohemite were purchased from DPSN Company. The DD3R crystals were coated on these supports via dip-coating method. The quality of the zeolite seed layer formed on the supports was investigated by SEM analysis. Then, the synthesis of DD3R zeolite membrane was carried out on the seeded support with optimized seeding concentration solution via hydrothermal treatment for growing the zeolite layer on the support. The XRD and SEM analyses were used to study the quality of the synthesized membrane layer. To investigate the separation performance of the synthesized DD3R membrane the permeation tests of gases such as N₂, CO₂ and CH₄ were carried out.

2- Experimental

2-1- Materials and Chemicals

The chemicals and materials used in this work were 1-adamantylamine (ADA, 97% Sigma-Aldrich), ethylene diamine (EDA, 99.5%, Merck), tetramethyl orthosilicate (TMOS, 98%, Merck) and deionized water. N₂, CO₂ and CH₄ with high purity were used for membrane permeation tests.

2-2- Morphology and Crystallinity

Scanning electron microscopy (SEM) was used to examine the microstructure and morphology of the seeded support and DD3R membrane and also to investigate the effective thickness. Surface roughness of the modified support was determined by Atomic force microscopy (AFM) analysis. XRD pattern of the synthesized DD3R zeolite membrane was collected by X-Ray diffractometer with Cu K-X-radiation to confirm the crystal phase.

2-3- DD3R Powder Synthesis

For preparing the reactant mixture, the amount of 1-adamantane amine was dissolved in ethylene diamine. Then, the calculated amount of deionized water was added to the solution under vigorous mixing for 1 h. After that, the solution was heated at 95°C under mixing for 1 h. The obtained solution was cooled and tetramethyl orthosilicate as silica source was slowly added. The resulting solution was heated again for 3 h at 95°C. The final solution with molar ratio of 100 SiO₂ : 11240 H₂O : 47 1-ADA : 404 EDA was poured into Teflon autoclave and followed by hydrothermal conditions (160°C with 60 rpm). The synthesized powder was centrifuged with deionized water to decrease the pH of the powder to neutral.

2-4- Seeding the Support

The supports were washed to remove dusts and impurities. Thereafter, they were dried at 90 °C for 3 h. After preparing the DD3R seeds and the supports, the seeds were coated on the surface of supports via dip-coating method by the following procedure. Three different concentrations of DD3R seed solutions (0.1, 0.2 and 0.3 wt% aqueous suspensions of the seeds) were prepared. Suspensions were stirred for 24 h at room temperature and followed by sonication to better dispersion and prevent the formation of aggregates. The prepared supports were immersed vertically into seeds suspensions for 240 s as dipping time and repeated for three times to obtain the high coverage of the support with DD3R crystals. After each dipping, the seeded supports were dried at 90 °C for 2 h.

2-5- DD3R Membrane Synthesis

The DD3R tubular membrane was synthesized by secondary growth method with hydrothermal treatment. The synthesis solution for membrane layer was prepared according to the section 1.3. Then, the resulting solution was poured into the Teflon autoclaves where the seeded support was placed in it and heated in an oven at 160 °C. The synthesized membrane was washed with deionized water until the pH of the washing water decreased to neutral. Before calcination in a furnace at 500 °C for 50 h, the membrane was dried at 45 °C for 48 h.

2-6- Single Gas Permeation Test

N₂ Gas permeation test was carried out as the primary test of the membrane layer before removal of structure directing agent (SDA). Because the SDA molecules were filled the zeolitic pores of DD3R. Therefore, a completely defect-free membrane has no permeance to any gases. The gas permeation test contains two sections including; feeding of the gases and separation of the gases (permeation cell). The membrane was sealed with O-ring in a stainless steel module. A schematic of the membrane module has shown in Figure 1. After the calcination process, the permeation test of the calcined membrane was carried out by using constant pressure method. A single gas of N₂, CO₂ and CH₄ was used as feed gases and fed outside of the zeolite membrane and the permeated flux of gas through the membrane was measured with a soap film flow meter.

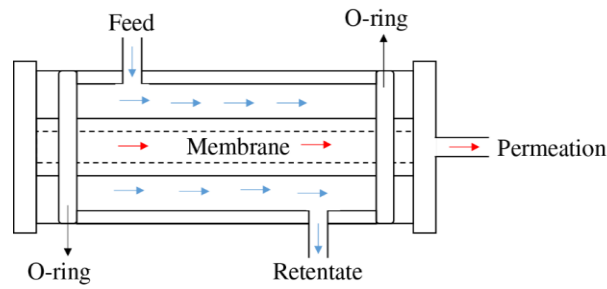


Figure 1. Schematic of membrane module.

3- Results and Discussion

Figure 2. shows the SEM analysis of α -alumina supports before and after modification. As smooth and uniform surface of supports is better for seeding, surface roughness of modified supports was measured by AFM analysis. Figure 3. illustrated the AFM analysis of the modified supports. By using Nano-surf software the average surface roughness for TiO_2 -bohemite as top layer was calculated ≈ 60 nm.

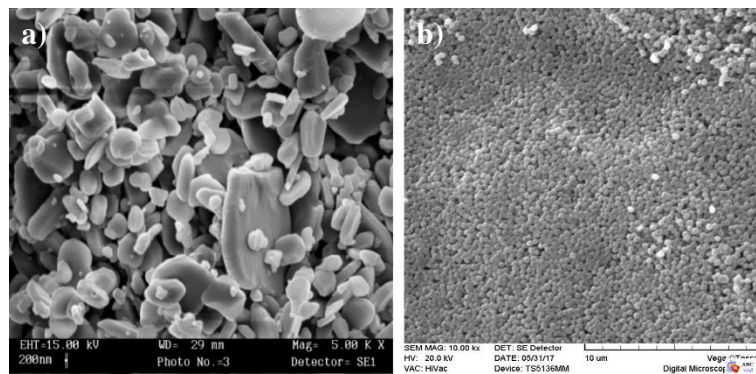


Figure 2. SEM images of α -alumina supports (a) before and (b) after modification by TiO_2 -bohemite.

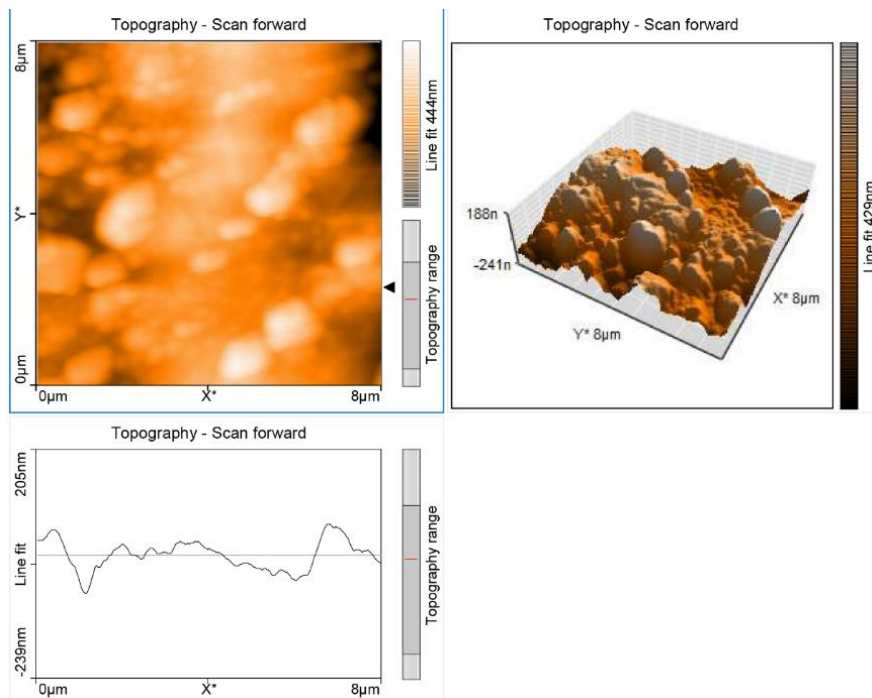


Figure 3. AFM analysis of the modified support.

Figure 4. shows the SEM images of the seeded support with 0.1, 0.2 and 0.3 wt% concentration of DD3R zeolite seeds solution. As shown in Figure 4 (a) and (c), there is a poor coverage of the seeds on the surface and some areas are without seed coverage. Thus, the formed layer is not uniform. According to Figure 4 (b), it is clear that an appropriate coverage for support has been obtained. These results indicate that seeding the support with 0.2 wt% concentration of seeds solution leads to the best and uniform coverage on the support.

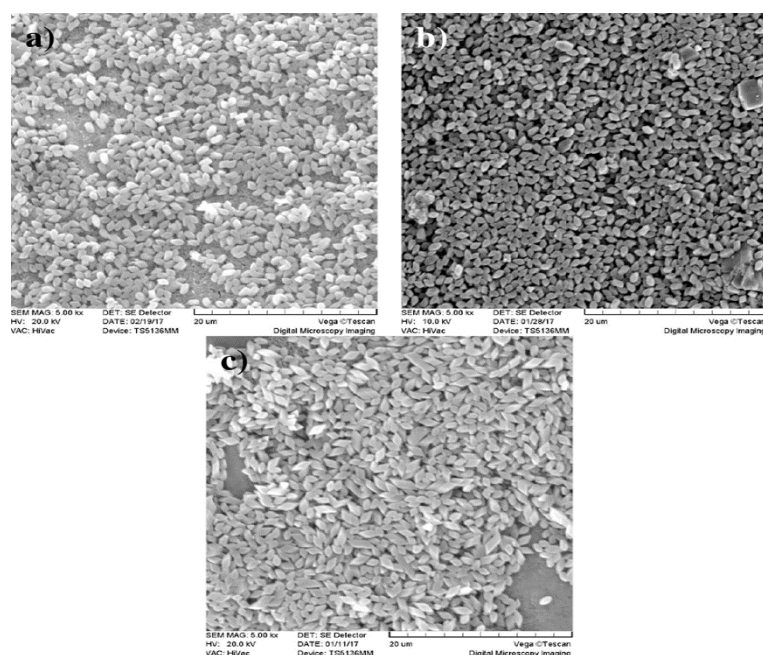


Figure 4. SEM images of the surface of seeded support with a) 0.1 wt% b) 0.2 wt% c) 0.3 wt% concentration of seeds solution.

Figure 5. depicts the XRD pattern of DD3R zeolite membrane obtained by hydrothermal treatment. As can be seen, all the major peaks of DD3R zeolite membrane has completely been formed. This pattern confirmed that the DD3R zeolite membrane prepared from DD3R seeds with 0.2 wt% concentration of zeolite seeds solution was formed on the modified support.

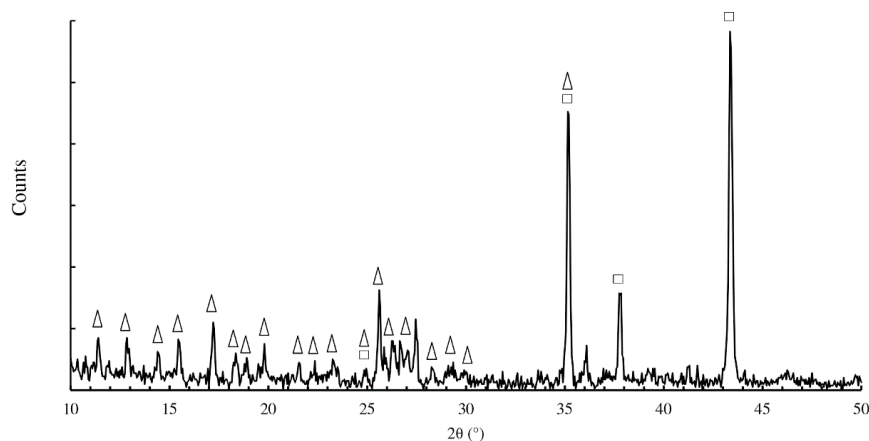


Figure 5. XRD pattern of the synthesized DD3R zeolite membrane.

Figure 6. shows the cross section and top view of the surface of the synthesized DD3R membrane. For the synthesis of this membrane, 0.2 wt% concentration of the seeds solution has been used. As can be seen, the uniform zeolite layer was formed on the surface support and this is due to the uniform distribution of the DD3R seeds on the modified support surface during seeding step. According to cross sectional SEM image, the thickness of DD3R layer is around 20 µm.

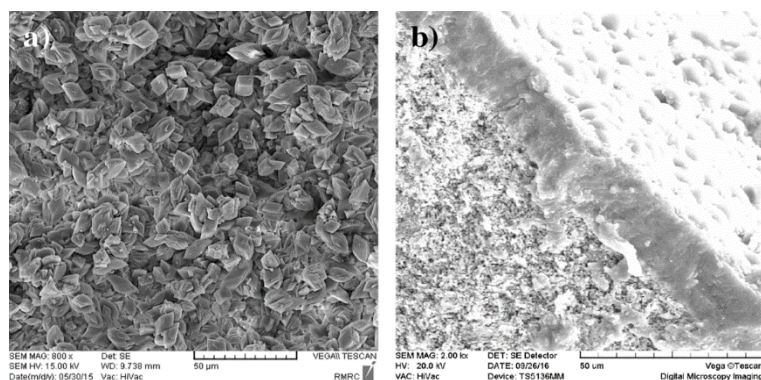


Figure 6. SEM images of the synthesized DD3R membrane (a) surface and (b) cross section.

Figure 7. showed the perm-selectivity of the synthesized DD3R membrane as a function of the feed pressure. As can be seen, the perm-selectivity of N_2 from CH_4 decreases at lower pressure range of 1 to 2 bar and remains approximately constant from 2 to 5 bar. Decreasing in perm-selectivity related to existence of some non zeolitic pores while these pores roles efficiently increase by increasing the pressure. This trend is also the same for the perm-selectivity of CO_2 from CH_4 . Also, the high perm-selectivity of CO_2 in comparison with N_2 is due to strongly adsorption of CO_2 on the DD3R zeolite over N_2 in the separation of natural gas impurities.

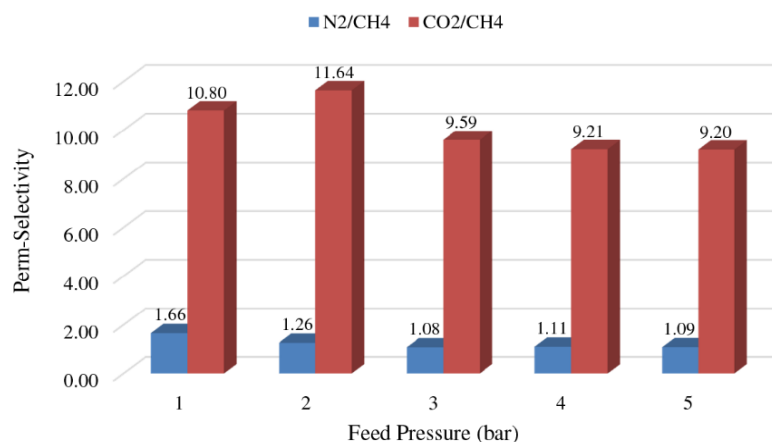


Figure 7. Comparison of the perm-selectivity of the CO_2/CH_4 and N_2/CH_4 through the DD3R membrane as a function of feed pressure at room temperature.

4- Conclusion

In this work, it is concluded that uniform DD3R zeolite seed layer can be formed on the modified surface of α -alumina support using dip coating method with 0.2 wt% seed suspension concentration. Synthesis of DD3R membrane layer on the seeded support with uniform seed layer induced formation of uniform zeolite layer. The single gas permeation results showed a good performance in separation of CO_2 from CH_4 . This synthesis procedure with optimized seed suspension concentration could have very promising results to achieve the selective DD3R zeolite membrane for natural gas purification.

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