SYNTHESIS AND CHARACTERISATION OF SULPHONIC ACID 3-MERCAPTOPROPYLTRIMETHOXYSILANE FUNCTIONALISED SILICALITE-1 MEMBRANE

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Abstract

10% and 20% of 3-mercaptopropyltrimethoxysilane was introduced into the silicalite-1 pore-structure by utilising in situ deposition method and subsequently oxidized to sulphonic acid silicalite-1 membrane. The resulting organic-inorganic hybrid membrane was characterized for its crystallinity and orientation (XRD), surface morphology and thickness (SEM) and elements present in the membrane (EDAX). Sulphonic acid functionalised silicalite-1 membrane is a new type of catalytic shape selective membrane which may be useful for combined separation and reaction process.

Keywords: Synthesis, Characterisation, Functionalised Silicalite-1 Membrane.

1. Introduction

Zeolite membranes or films have been well known of their well-defined micropore structure, good thermal and structural stability, high mechanical strength, feasible for steady-state operation, low energy consumption, resistance to relatively extreme chemical environment and great potential for combined steps of reaction/separation [1-6]. Zeolites are crystalline, microporous aluminosilicates which find extensive industrial uses as catalysts, adsorbents, and ion exchangers with high capacities and selectivities [7-8]. When zeolites are grown as films, zeolite membrane is formed. The characteristics of zeolite membrane have found its new application in gas, vapour and liquid separation especially in petrochemical industry based on their properties adsorption,

preferential diffusion, or pure molecular sieving (size exclusion) [9]. Besides, membranes composed of different type of zeolites provide different framework structure and pore size, which make it suitable for application in membrane reactors, catalytic membrane reactor, sensitive chemical sensors, reactive and non-reactive gas sensors, electronic and thermoelectronic applications such as zeolite based capacitors [2, 10]. Currently, zeolite membranes have been found of its promising application field in corrosion protection and antimicrobial coatings [10].

In the past few years, an extensive study of synthesis of zeolite membrane especially MFI (ZSM-5 and silicalite-1) zeolite membrane was performed by various researchers; because of its pore structure is near to the sizes of many industrially important organic molecules. As shown in Fig. 1, zeolite MFI has the pore structure of straight (b-oriented), circular pores (0.54 x 0.56 nm) interconnected with sinusoidal (a-oriented), elliptical pores (0.51 x 0.54 nm) and a tortuous path along the c-direction [11]. For the application in gas or liquid separations, the membrane performance is described by permeance/flux and separation factor which are highly related to the membrane microstructure and orientation. Therefore, the way to control the membrane microstructure and orientation is highly desirable.
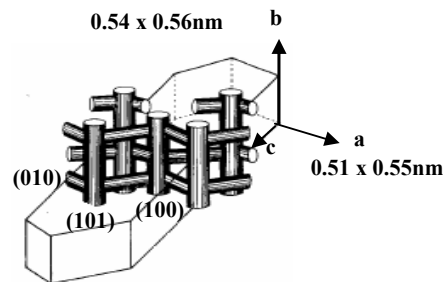

Fig. 1. 3-Dimensional Pore Structure of MFI Zeolite [11].

In the recent years, researchers have explored the possibility of adding chemical function into the pores of zeolites with organic groups, result in organic-functionalised molecular sieves material which is crystalline with inorganic frameworks and pendant organic groups in the pores. The organic functional groups confined within the micropores of the zeolites could be utilised as shape-selective catalysts for number of industrial important reactions [12-18]. Therefore, the solid-catalyst, acid functionalised zeolite crystal, has been the subject of many researchers because of safety, low cost and ease of recovery derived from the heterogeneous catalysis [16]. The modification of such materials by organic functional molecules will also greatly broaden their usefulness [17].

The first synthesis of a shape-selective organic functionalised molecular sieve (OFMS) has been reported by Jones et al. [12]. The detailed synthesis and characterisation of crystalline, organic-functionalised molecular sieves having zeolite BEA (beta) topology was achieved, where the functional groups, such as phenethyl (PE), ethylcyclohexenyl (CHE) and mercaptopropyl (MP) covalently adhered within the micropores. These functional groups were sulfonated to

produce a microporous solid containing intracrystalline sulfonic acids, which was transformed into solid catalyst. These materials have shown to be an effective shape-selective catalysts for various reactions based on organic active sites and these active sites could be tailored to meet the needs of the reaction interest [12, 17].

Although the shape-selective organic functionalised zeolite BEA (beta) crystals with different type of functional group were successfully synthesised, the development of acid functionalised zeolite membrane still remains a new task. This relative new membrane material having a large potential to be used as shape selective catalyst as well as other application, depending on the functional group. However, problems do exit in order to develop the membrane:

1. amorphous impurities; in order to obtain highly crystalline membrane, optimum organic group deposited into the zeolite membrane framework need to be figured out.
2. the pores tended to be blocked by the organic functional groups (only high-silica zeolite will be prepared, e.g. silicalite-1)

Before emphasising its applications, it is crucial to know how to develop this new type of membrane. From the literature, for successful and effective application in separation, the orientation of the zeolite crystal in the membrane is important. For reaction studies, development of shape selective catalyst is needed. Therefore, in the present work, we had demonstrated b-oriented, organic-functionalised zeolite MFI membrane which may be useful in combined separation and reaction process. In order to avoid pore-blocking by organic functional groups and to obtain highly crystalline functionalised membrane, a detailed investigation of the synthesis of silicalite-1 (pure silica zeolite MFI) membrane with 10% and 20% loading of 3-mercaptopropyltrimethoxysilane (3MP) organic functional group are performed. The membranes were subsequently oxidised to sulphonic acid 3MP functionalised silicalite-1 membrane by using aqueous H_2O_2 as an oxidising agent. The membranes were further characterised for its crystallinity, morpohology, thickness and element composition by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray (EDAX).

2. Experimental Procedures

In situ deposition method was utilised to incorporate organic functional group into silicalite-1 framework. In situ deposition method is the most common method used by the researchers where the functional groups are introduced in the synthesis solution as silica source [12-16]. First, a homemade porous α-alumina support (diameter = 25 mm, thickness = 3mm) was coated with a thin mesoporous layer using sol-gel technique developed by Brinkers and co-workers [1]. The role of mesoporous layer is to improve the structural stability, reduce the mismatch between zeolite membrane and support during calcination and serve as a support for a microporous membrane [1, 19].

3-mercaptopropyltrimethoxysilane (3MP) functionalised silicalite-1 membrane with 10% and 20% 3MP compositions were synthesised based on the procedure reported by Lai et al. [19] for nonfunctionalised zeolite siliceous ZSM-5. 3MP functionalised silicalite-1 membranes were synthesised using tetraorthosilicate (TEOS) as silica source and 3MP as organosilicon source. The

synthesis solution was prepared by adding 4g of tetrapropylammonium hydroxide (TPAOH, 1M, prepared by ion-exchange with tetrapropylammonium bromide (TPABr, 1M, Merck) using strong OH⁻ resin) to a polypropylene bottle containing a magnetic stir bar and 72g double deionised water (DDI H_2O). Appropriate amount of TEOS (> 98%, Merck) was added drop wise and the solution was stirred gently. Then, an appropriate amount of 3MP (85%, Acros) was added slowly to complete the reaction mixture. The final molar composition of any given synthesis solution was: $(1-x)$TEOS: TPAOH: 500 H_2O: x(3MP), where x is molar composition and $x = 0.0$, 0.1 and 0.2 in the present studies. For synthesis of non-functionalised silicalite-1 membrane, $x = 0$. The reaction mixture was then stirred vigorously for 1 day in room temperature. After vigorous stirring, the synthesis solution was transferred into Teflon-lined autoclave containing a α-alumina support coated with mesoporous layer, which was place horizontally inside the Teflon-lined with the aid of Teflon support holder. The autoclave was sealed and placed inside a hydrothermal Parr reactor and heated to 175°C for 1 day. After 1 day, the membrane was taken out, repeated washed with DI water and dried in oven at 100ºC overnight. In order to make sure the membrane was fully coated on the support, nitrogen permeance test was performed on the membrane by using permeability measurement test rig before removal of template (TPAOH). Hydrothermal synthesis of membrane was repeated until the membrane was impermeable to nitrogen. Finally, the functionalised membrane was calcined at 420ºC for 15 h with a heating and cooling ramping rate of 0.5ºC/min. 3MP functionalised silicalite-1 membranes were oxidised to sulphonic acid by utilised the method as described by Jones et al. [13] The membrane was placed inside the Teflon-liner with the aid of Teflon support holder where the functionalised membrane was facing downward. After treated with 30% H_2O_2 for 24 h, the membrane was washed with DI water and soaked in 0.1 M H_2SO_4 for 4 h. The membrane was washed with DI water and dried at 100ºC overnight. Both of the seeds and membranes were stored in a desiccator before characterisation.

The crystallinity and orientation of the prepared samples was obtained by XRD analysis using PANanalytical X-Pert PRO X-ray diffractometer with CuK_α radiation ($\lambda = 1.5406 \overset{0}{A}$) operated at 40 kV and 30 mA in the range of $5^o \leq 2\theta \leq 50^o$. The morphology and thickness of the membranes were studied using Zeiss Supra 35VP scanning electron microscope (SEM). The SEM analysis was extended to obtain quantitative composition of elements on the surface under energy dispersive X-ray instrument (EDAX, INC). EDX Quantification software was used to calculate the elemental composition and the Si/S ratio of the functionalised membrane.

3. Results and Discussion

Hydrothermal synthesis at 175ºC for 1 day has been applied to synthesis silicalite-1 membrane and 3MP-functionalised silicalite-1 membrane. Post-synthesis modification has been done to oxidise the functional group to sulphonic acid group. 0.9 TEOS/0.1 3MP is named as silicalite-1-3MP-10 and silicalite-1-SO₃H-10 after oxidation. Two samples with different 10% and 20% 3MP content were prepared and for comparison, non-functionalised silicalite-1 membrane was also prepared. Fig. 2 shows the XRD pattern for the three membranes. As shown in Fig. 2a, silicalite-1 membrane was highly crystalline after 24 h synthesis duration

at 175°C. Its XRD pattern shows the presence of all the major peaks for MFI (ZSM-5 or Silicalite-1) zeolite, which is consistent to the MFI zeolite reference XRD pattern given by the International Zeolite Association (IZA) [20]. Most of the crystals in silicalite-1 membrane were oriented with their b-axis perpendicular to the support surface, (020), (040) and (060). However, there was a fraction of crystals which were not preferentially oriented and their presence shows the peak (101) in the XRD pattern. From the integrated peak intensity, we found that about 62% of the crystals in the membrane were oriented in b-axis.

Figure 2b shows the XRD pattern for silicalite-1-3MP-10 membrane and highly crystalline membrane was also found, as comparable to silicalite-1 membrane. This explains that the 3MP functionalised silicalite-1 membrane was formed under the same synthesis condition. In Fig. 2b also, there were peaks coming from S and SiC which show the incorporation of 3MP into the silicalite-1 framework. XRD pattern for silicalite-1-3MP-20 membrane is shown in Fig. 2c and its show that the membrane was not formed due to absence of the typical peaks for silicalite-1 membrane in the range of 5° to 26°. The peaks belong to α – alumina support and amorphous materials (SiC and S) were present can conclude that once the mol % of organic group incorporated into the zeolite framework increased, the crystallinity of the zeolite reduced, and thus membrane could not be formed.

Figure 3a shows the SEM micrograph for blank α-alumina support layer. After coated with mesoporous silica layer, a smooth and continuous layer is formed on top of the support and the micrograph is shown in Fig. 3b. As shown in Fig. 3d, the thickness of mesoporous layer was 8 μm on the support surface, while some deposition inside the support pores also took place. The SEM images for the silicalite-1 membrane are shown in Fig. 3c. The typical coffin-like shaped crystals of silicalite-1 were obtained and most of the crystals were oriented with b-axis, faced parallel to the support surface. The micrograph shown in Fig. 3c is consistent with the XRD pattern shown in Fig. 2a, where there were still small portion of the crystals oriented in others direction. The cross-section of the membrane is shown in Fig. 3d, where the membrane thickness obtained in this work was 16 μm.

The SEM micrographs of silicalite-1-3MP-10 membrane are shown in Fig. 4a. The coffin-like shape of the crystals was retained even in the presence of the amorphous materials. The addition of 3MP to the synthesis composition did not lead to formation of smaller crystals, but modified the crystal morphology. The variation of morphology confirmed that the 3MP exerted a definite effect upon the crystallisation of functionalised zeolite. After oxidation, the SEM micrographs of silicalite-1-SO_3H-10 membrane are shown in Fig. 4b. It can be seen that no obvious changes in the membrane's morphology before and after oxidation. Functionalised crystal aggregates were present on the membrane surface and no cracks were observed on the membrane. From the micrographs also, the orientation of the crystals was consistent with the XRD pattern (Fig. 2b), where most of the crystals were also oriented in b-axis. Fig. 4d shows the SEM micrograph of silicalite-1-3MP-20. Large portion of the support surface still did not cover with functionalised crystals although hydrothermal synthesis of membrane was repeated for five times. The crystals were not grown while a large quantity of amorphous materials agglomerated on the support causing the membrane layer was not formed. The result obtained from SEM micrograph was

also consistent with membrane's XRD pattern. Figure 4c shows the cross section of the membrane and the thickness of the silicalite-1-3MP-10 membrane was 7μm. Therefore, in the present study, it was observed that the functionalised silicalite-1 membrane with 20% of 3MP was not formed.
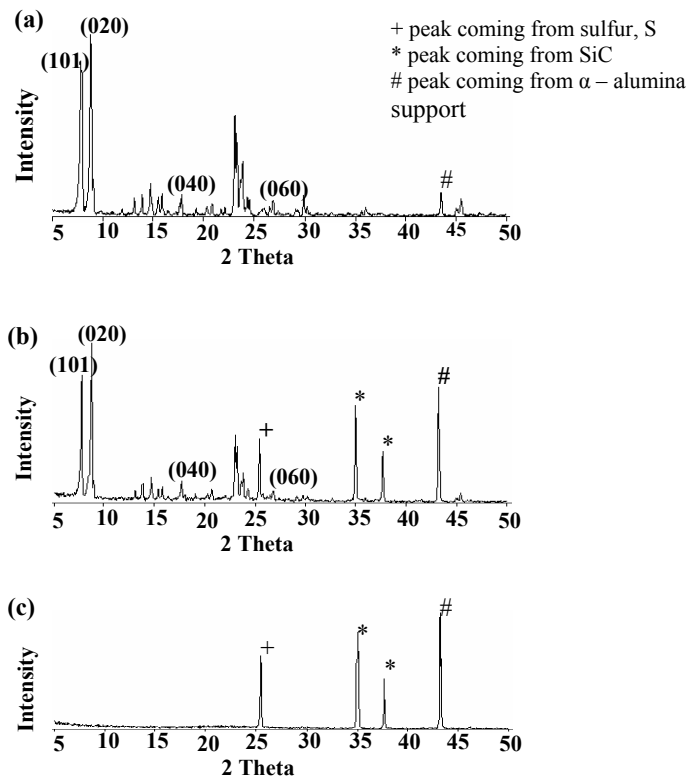

Fig. 2. XRD Pattern for (a) Silicalite-1 (b) Silicalite-1-3MP-10 and (c) Silicalite-1-3MP-20 Membranes.

The aim of EDX analysis was to determine the composition of elements in silicalite-1 and silicalite-1-SO_3H-10 membranes. EDX spectrum for the membranes are shown in Fig. 5. Strong Si and O peaks were observed in Fig. 5a, which are the typical elements present in the silcialite-1 membrane. For silicalite-1-SO_3H-10 membrane, a small C peak and a small S peak were observed in Fig. 5b. Both C and S peaks came from the 3MP groups, which were introduced into the silicalite-1 framework during in situ deposition in hydrothermal synthesis. The Si/S ratio of the membrane was 9, was slightly deviated from the chemical composition of the synthesis solution, which was 10. This shows that 90% of the 3MP groups were successfully incorporated into the silicalite-1 frameworks. The EDX spectrums had confirmed the presence of 3MP groups in silicalite-1-SO_3H-10 membrane.
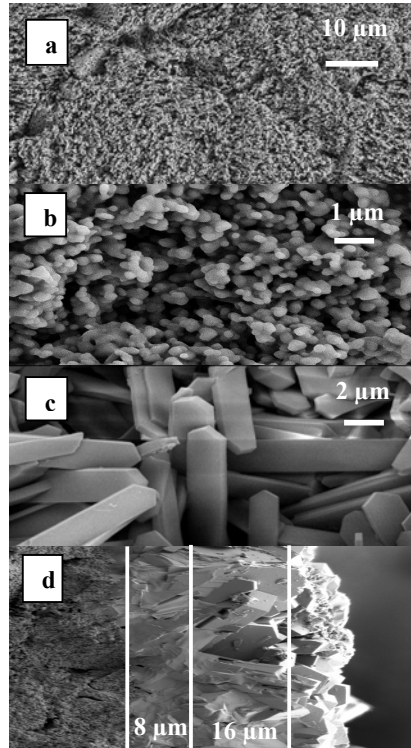
Fig. 3. SEM Micrographs for (a) Blank α-Alumina Support, (b) Mesoporous Layer, (c) Silicalite-1 Membrane and (d) Cross Section.

4. Conclusions

In conclusion, organic functionalised silicalite-1 membrane with 10% of 3 mercaptopropyltrimethoxysilane (3MP) loading was successfully synthesised after hydrothermally treated at 175°C for 1 day. The characterisations show that 90% of the 3MP groups were incorporated into the silicalite-1 framework and 62% of the crystals were oriented in b-axis. The membrane was oxidised to sulphonic acid membrane resulted in sulphonic acid 3MP silicalite-1 membrane which could be used in combined separation and reaction studies. Beside 3MP, further studies are needed to figure out the possibilities of synthesis of other types of organic functionalised silicalite-1 membrane. The application and performance of these functionalised membranes need to be investigated
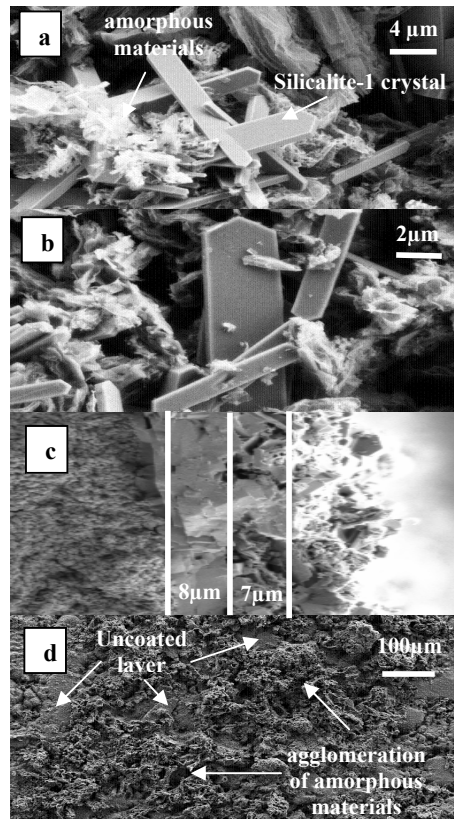
Acknowledgements

Fig. 4. SEM for functionalised membrane, (a) silicalite-1-3MP -10, (b) silicalite-1-SO$_3$H-10, (c) silicalite-1-SO$_3$H-10 membrane thickness and (d) silicalite-1-SO$_3$H-20.
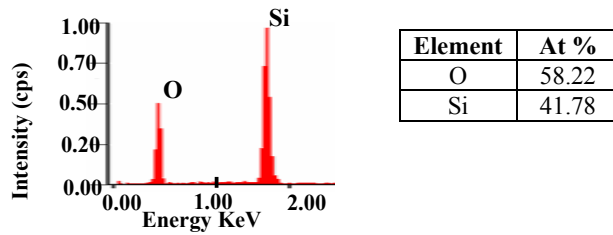

Element	At %
O	58.22
Si	41.78

Fig. 5a. EDX Results for Silicalite-1 Membranes.

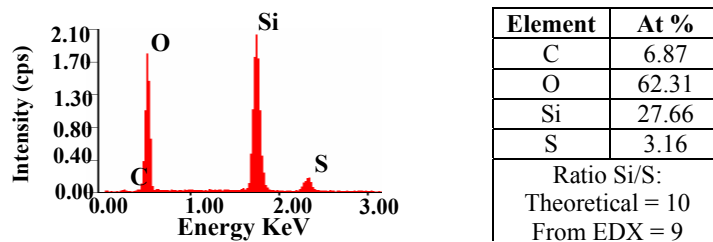| Element	At %
C	6.87
O	62.31
Si	27.66
S	3.16
Ratio Si/S: Theoretical = 10 From EDX = 9	

Fig. 5b. EDX Results for Silicalite-1-SO₃H-10 Membranes.

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