CHAPTER 4 FABRICATION AND CHARACTERIZATION OF SUPPORT SYSTEMS

4.1. INTRODUCTION

For removal of VOCs from water & air using nanoparticles, a support system is required. This chapter discusses the fabrication and characterization of support systems used to immobilize the nanoparticles. Two types of support systems, polymer membrane support as well as ceramic support (alumina based) are fabricated and characterized to study their surface properties. These support systems are embedded with the nanoparticles such as Fe6-Ni, FMO, CTO & NTO. Various techniques like dip coating, adding the nanoparticles during fabrication and in-situ immobilization are used to immobilize the nanocatalysts onto the support.

4.2. POLYSULFONE MEMBRANE SUPPORT SYSTEM

Membranes based on Polysulfone (PSf) (average mol. Wt. 75,000) were fabricated using phase inversion technique with N-Methylpyrrolidone (NMP) as solvent and Polyvinylpyrrolidone (PVP) (average mol. Wt. 40,000) as pore former.

4.2.1. Preparation of Base Polysulfone Membrane

PSf membranes with concentration of 5%, 10%, 15% and 20% are fabricated as given in the following sections.

4.2.1.1. 5% PSf Membrane

5% PSf membrane was fabricated by dissolving 1.0 g PSf in 18 g of NMP (17.5 ml, ρ=1.028) maintained at 60°C under periodic stirring till a homogeneous mixture is
formed. To this homogeneous mixture 1.0 g PVP was added and kept still until the solution becomes homogeneous and viscous. This homogeneous mixture was then casted onto a glass plate using an Elcometer. These plates were then immersed in DI water for 24 hrs to completely dissolve all the PVP and NMP. The membrane was then air dried at room temperature for 24 hrs.

4.2.1.2. 10% PSf Membrane

10% PSf membrane was fabricated by dissolving 2.0 g PSf in 16 g of NMP (15.5 ml, $\rho=1.028$) maintained at 60°C under periodic stirring till a homogeneous mixture is formed. To this homogeneous mixture 2.0 g PVP was added and kept still until the solution becomes homogeneous and viscous. This homogeneous mixture was then casted onto a glass plate using an Elcometer. These plates were then immersed in DI water for 24 hrs to completely dissolve all the PVP and NMP. The membrane was then air dried at room temperature for 24 hrs.

4.2.1.3. 15% PSf Membrane

15% PSf membrane was fabricated by dissolving 3.0 g PSf in 14 g of NMP (13.5 ml, $\rho=1.028$) maintained at 60°C under periodic stirring till a homogeneous mixture is formed. To this homogeneous mixture 3.0 g PVP was added and kept still until the solution becomes homogeneous and viscous. This homogeneous mixture was then casted onto a glass plate using an Elcometer. These plates were then immersed in DI water for 24 hrs to completely dissolve all the PVP and NMP. The membrane was then air dried at room temperature for 24 hrs.

4.2.1.4. 20% PSf Membrane

20% PSf membrane was fabricated by dissolving 4.0 g PSf in 12 g (11.5 ml, $\rho=1.028$) of NMP maintained at 60°C under periodic stirring till a homogeneous mixture is formed. To
this homogeneous mixture 4.0 g PVP was added and kept still until the solution becomes homogeneous and viscous. This homogeneous mixture was then casted onto a glass plate using an Elcometer. These plates were then immersed in DI water for 24 hrs to completely dissolve all the PVP and NMP. The membrane was then air dried at room temperature for 24 hrs.

4.2.2. Characterization of PSf membranes

All the four PSf membranes are characterized using FESEM to find out the morphology, pore size and pore distribution. Fig. 4.1 shows the FESEM images of these PSf membranes. The pore size of these PSf membranes are given in table 4.1.

Figure 4.1: FESEM images of A - 5%, B - 10%, C - 15% & D - 20% PSf membranes
Table 4.1: Pore size of PSf membranes

<table>
<thead>
<tr>
<th>PSf Concentration (Wt%)</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (μm)</td>
<td>48</td>
<td>4.8</td>
<td>0.102</td>
<td>0.08</td>
</tr>
</tbody>
</table>

A graph plotted between PSf concentration and the pore size is shown in fig. 4.2. It is evident that there is a reduction in the pore size with increase in concentration of PSf.

![Figure 4.2: Graph showing the relation between Pore size and Concentration of PSf](image)

15% PSf membrane is chosen for immobilization of the nanoparticles as the pore size of this membrane is in close co ordinance with that of the nanoparticles. 20% PSf membrane is has a better pore size but from the FESEM image, it is observed that the pore volume is very low.
4.3. NANOPARTICLE IMMOBILIZED PSF MEMBRANE

Various techniques were tried to immobilize the nanoparticles onto the porous membrane including dip coating, adding nanoparticles to the polymer cast solution and in-situ immobilization. From the analysis results it was found that the in-situ immobilization technique gave better performance and less leaching of the nanomaterials.

4.3.1. Dip coating

15% PSf membrane was used for dip coating. A dry membrane was dipped in Fe-Ni nanoparticle dispersed in ethanol for about 1 hr, then air dried at room temperature for 12 hrs and then at 80°C for 12 hrs. Fig. 4.3 presents the FESEM image of the PSf membrane. From the image it is found that agglomeration of Fe-Ni nanoparticles over the surface of the membrane, which means the nanoparticles, are not uniformly coated over the membrane. So, PSf membranes immobilized with nanoparticles using dip coating method are not suitable.

Figure 4.3: FESEM image of PSf membrane dip coated with Fe-Ni nanoparticles
4.3.2. Adding nanoparticles to PSf cast solution

The polysulfone cast solution was made by dissolving 15wt% of PSf (3.0 g) in 14.0 g NMP (14.0 ml, $\rho=1.028$) with 15wt% PVP (3.0 g) as a pore former [64, 65]. To this homogeneous solution, Fe-Ni nanoparticles were added and mixed thoroughly. The bimetallic nanoparticle immobilized PSf matrix is fabricated by casting this solution onto a clean and dry glass plate using an Elcometer with a thickness of 100 $\mu$m. After casting, the matrix was immersed in still DI water and kept overnight to ensure formation of a microporous support and to completely remove the NMP and PVP.

Fig 4.4 shows the FESEM image of Fe-Ni nanoparticles immobilized PSf membrane. The polysulfone matrix act as a solid support for the Fe-Ni nanoparticles and the support increases the available reactive metal surface area for the reaction to take place [66]. But, from the FESEM image it is evident that there is considerable agglomeration of the nanoparticles over the membrane surface.

Figure 4.4: FESEM images showing the surface of nanoparticle immobilized membrane
The EDS analysis reported in Fig. 4.5, shows the presence of iron and nickel particles in their elemental state and there is prominent amount of sulfur and oxygen due to the presence of sulfone group in polysulfone.

![Figure 4.5: EDS analysis of Fe-Ni nanopartilce immobilized membrane](image)

**4.3.3. In-situ Immobilization**

**4.3.3.1. Preparation**

In in-situ immobilization, the nanoparticle precursors are added to the solvent NMP in required stoichiometric quantities, mixed with PSf and PVP and when the mixture turns homogeneous, casted onto glass plate and dipped in water mixed with a reducing agent. The precursors ions are reduced into zero-valent state and the by-products are washed out along with the pore former (PVP).

0.2 g of ferric chloride (FeCl₃ 6H₂O) and 0.1 g of nickel chloride (NiCl₂ 6H₂O) were dissolved in 13.75 g (13.5 ml, ρ=1.028) of NMP and to this homogeneous mixture 3.0 g of PSf (15%) was added and the mixture was maintained at 60°C till PSf is completely dissolved. To this homogeneous solution 3.0 g of PVP (15%) was added and stirred until
complete dissolution and then kept still for some time to avoid air bubbles in the formed viscous solution. Then this homogeneous polymer solution is casted onto a glass plate using an Elcometer and the plate was immersed in water mixed with 5 g sodium borohydride (NaBH₄) for 15 min and then in DI water for 24 hrs. The membrane was then air dried at room temperature for 24 hrs.

4.3.3.2. Characterization

Fig. 4.6 presents the FESEM images of the membrane in-situ immobilized with Fe-Ni nanoparticles. From the FESEM image it can be observed that the nanoparticles are spread all over the membrane without any agglomeration. The pores are very distinctive and uniformly distributed all over the surface. Powder XRD pattern of the membrane is recorded to study the nanoparticle formation.

Figure 4.6: FESEM image of PSf membrane in-situ immobilized with Fe-Ni nanoparticles
Fig. 4.7 gives the XRD pattern, all the prominent peaks at 44.2639°, 64.3947°, 77.3170° and 81.4025° which closely correspond to simple cubic Fe-Ni (JCPDS # 88-1715). A huge signal is found in the range of 15 – 30°, which corresponds to carbon present in PSf.

![XRD pattern of PSf membrane in-situ immobilized with Fe-Ni nanoparticles](image)

Figure 4.7: XRD pattern of PSf membrane in-situ immobilized with Fe-Ni nanoparticles

### 4.3.4. Specific Surface Area and Porosity

The BET analysis (analysis of N₂ adsorption/desorption isotherm) plots shown in fig. 4.8, reveals that the as PSf membrane in-situ immobilized with Fe-Ni nanoparticles have a high surface area ($S_{BET}$) of 22.8584 m²/g. It was also noticed that the material has a high pore volume of 0.047 cm³/g and median pore width of 36.56 nm and a narrow size distribution of pores.
4.3.5. Stability of Fe-Ni Nanoparticles in PSf Membrane

Stability of Fe-Ni nanoparticles in the polysulfone matrix was studied using inductively coupled plasma mass spectrometer (ICPMS). To measure the amount of Fe-Ni eluted from the matrix fabricated by In-situ immobilization method, DI water was passed continuously through Fe-Ni nanoparticle immobilized polysulfone matrix and the water samples are collected for every 12 hrs for the two consecutive days. The water samples were analyzed to check the leaching of the Fe-Ni nanoparticles.

In ICPMS, water sample is converted into aerosol and inserted into plasma. The most common plasma used is argon plasma. Any metal molecules present in the aerosol are instantaneously ionized and these ions are detected and quantified using a mass spectroscope. The detection limit is 0.005mg/L. The ICPMS data in Table 4.2 shows that the concentration of Fe-Ni nanoparticles in the water is below the detection limit of the instrument for all the samples. The leaching of Fe-Ni nanoparticles from the PSf membrane matrix is negligible.
Table 4.2: ICPMS analytical data of water samples

<table>
<thead>
<tr>
<th>Time</th>
<th>Test material</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 hr</td>
<td>Fe &amp; Ni</td>
<td>BDL (DL: 0.005mg/l)</td>
</tr>
<tr>
<td>24 hrs</td>
<td>Fe &amp; Ni</td>
<td>BDL (DL: 0.005mg/l)</td>
</tr>
<tr>
<td>36 hrs</td>
<td>Fe &amp; Ni</td>
<td>BDL (DL: 0.005mg/l)</td>
</tr>
<tr>
<td>48 hrs</td>
<td>Fe &amp; Ni</td>
<td>BDL (DL: 0.005mg/l)</td>
</tr>
</tbody>
</table>

BDL - Below Detection Limit

4.4. ALUMINA BASED CERAMIC SUPPORT

Alumina was chosen as the ceramic support for impregnation of nanomaterials because of its unique properties like chemical inertness, high thermal conductivity, high melting point etc. Alumina was synthesized following Sol-Gel route.

4.4.1. Fabrication of alumina support

Al₂O₃ support was fabricated by boehmite sol (Aluminum oxide hydroxide) method. Boehmite sol was made by controlled precipitation of aluminum nitrate (Al(NO₃)₃.9H₂O) solution. To this aluminium nitrate solution maintained at 90°C, dilute ammonium hydroxide solution is added very slowly avoiding rapid precipitation. The pH was maintained at 8 resulting in the formation of a milky white solution. This solution is then left for stirring till a white precipitate is formed. This precipitate is then washed several times with hot DI water, to remove the by-products like nitrates of ammonium.

The precipitate is then dissolved in DI water and treated with 20% aqueous nitric acid till the pH of the solution is in the range of 3-3.5. Upon reaching the appropriate pH, the mixture turns into a colloidal sol. This sol is then left for aging under mild stirring at 80°C till it turns into a gel (Boehmite). This gel is then calcined at 1050°C for 6 hrs.
4.4.2. Characterization of alumina support

From the powder XRD pattern of the alumina support given in fig 4.9, it is found that the support is highly crystalline with multiple crystalline phases present. The XRD pattern matches well with the JCPDS pattern # 46 – 1131 of tetragonal alumina.

![XRD pattern of alumina support](image)

**Figure 4.9: XRD pattern of alumina support**

From the FESEM image of calcined alumina based ceramic support shown in Fig 4.10; it is observed that the alumina particles are in size range of 2 – 30 μm and are mostly uniform. The surface has few defects, i.e., surface cracks which can be due to the calcination procedure. The sample surface looks mesoporous with a lot of inter granular spaces.
Figure 4.10: FESEM image of alumina support

The BET analysis (analysis of N\textsubscript{2} adsorption/desorption isotherm) plots shown in Fig 4.11, revealed that the alumina support is mesoporous in nature. The adsorption isotherm plotted between quantity of gas adsorbed and relative pressure of adsorption (P/P\textsubscript{0}), matches with type IV isotherm indicating that the material is highly porous and the pore radius will be in the range of 1.5 – 100 nm. From the BET surface area plot obtained from fraction of gas adsorbed by a monolayer of the material and the relative pressure of adsorption, given in fig. 4.12, it is found that alumina has a specific surface area (S\textsubscript{BET}) of 95.14 m\textsuperscript{2}/g. It is also noticed that the material has a high pore volume of 0.045 cm\textsuperscript{3}/g and average pore diameter of 101.5 nm and a narrow size distribution of pores.
Figure 4.11: N\textsubscript{2} adsorption isotherm Plot of alumina support

Figure 4.12: Specific surface area plot of alumina support
Apparent porosity of alumina support is calculated using the evacuation method. The support is cut into a 6.5 cm * 6.5 cm * 4.0 cm piece and dried at 100°C in a hot air oven to remove all adsorbed moisture and other vapors. This dry piece is weighed and the weight is taken as dry weight \( D \) (17.6549 g). The dry support piece is then immersed in water and boiled for 2 hrs at 80°C and then the specimen is taken out of water, and the soaked weight \( W \) (19.8668 g) is measured. Then the specimen is suspended in water using a sting attached to the weighing balance and the suspended weight \( S \) (14.6831 g) is measured. From these values the apparent porosity \( P \) is calculated using equation 4.1

\[
P = \frac{W - D}{W - S} \times 100 \% \tag{4.1}
\]

where

- \( P \) - Apparent porosity
- \( W \) - Soaked weight of the specimen
- \( D \) - Dry weight of the specimen
- \( S \) - Suspended weight of the specimen

From the calculation it is found that the alumina support has an apparent porosity of 43.13%.

**4.4.3. Characterization of Alumina supports Immobilized with Nanoparticle**

Nanoparticles are impregnated onto alumina by adding the FMO, CTO and NTO nanoparticles seperately to the boehmite sol. The sol was stirred for about 6 hrs to ensure uniform dispersion of the nanoparticles and then the sol is heat treated at 100°C till gel is formed; this gel is then transferred into a crucible and is calcinated at 1050°C.

Fig. 4.13 presents the FESEM images taken to find the morphology of the alumina support. From the image it can be observed that the support surface has uniformly distributed grains in the size range of 0.2 – 3 \( \mu \text{m} \). EDS analysis is performed to study the
elements present on the support surface and the EDS plot is given in fig. 4.14. Table 4.3 gives the elemental weight percentage from EDS analysis.

Figure 4.13: FESEM image of FMO nanoparticles coated alumina support

Figure 4.14: EDS analysis of alumina support impregnated with FMO nanoparticles
Table 4.3: Elemental weight % report of alumina support impregnated with FMO nanoparticles

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>48.42%</td>
</tr>
<tr>
<td>Al</td>
<td>11.76%</td>
</tr>
<tr>
<td>C</td>
<td>24.30%</td>
</tr>
<tr>
<td>Cl</td>
<td>3.04%</td>
</tr>
<tr>
<td>Fe</td>
<td>6.76%</td>
</tr>
<tr>
<td>N</td>
<td>1.77%</td>
</tr>
<tr>
<td>Mn</td>
<td>2.49%</td>
</tr>
<tr>
<td>Na</td>
<td>1.46%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100%</strong></td>
</tr>
</tbody>
</table>

From the elemental weight percentage analysis it can be observed that there is a dominant quantity of oxygen present in the sample, which is justified as both alumina and FMO have a high stoichiometric ratio of oxygen in them. The presence of Fe and Mn along with Al indicates the presence of aluminum, iron and manganese. A significant percentage of carbon is seen the analysis as a carbon tape is used to fix the sample to the sample stud.

To study the distribution of FMO nanoparticles onto alumina support, EDS mapping is performed. Fig. 4.15 shows the EDS mapping image of FMO nanoparticle immobilized alumina support. The image gives the distribution of aluminum (Al) represented in Al-K, oxygen (O) represented in O-K, iron (Fe) represented in Fe-K and manganese (Mn) represented in Mn-K. From the image it is evident that the elements are distributed all over the surface of the support.
Figure 4.15: EDS mapping of FMO nanoparticle immobilized alumina

Figure 4.16 presents the FESEM image of calcined alumina support coated with CTO nanoparticles. From the image it can be observed that the support surface has uniformly distributed grains in the size range of 0.2 – 5 μm. Mild agglomerations are found on the surface, which might be caused due to the cintering temperatures. EDS analysis is performed to study the elements present on the support surface and the EDS plot of CTO immobilized alumina support is given in fig. 4.17, the weight percentage of the elements is given in Table 4.4.
Figure 4.16: FESEM image of CTO nanoparticles coated alumina support

Figure 4.17: EDS analysis of clay support impregnated with CTO nanoparticles
Table 4.4: Elemental weight % report of clay support impregnated with CTO nanoparticles

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>59.12%</td>
</tr>
<tr>
<td>Al</td>
<td>28.12%</td>
</tr>
<tr>
<td>Ti</td>
<td>21.51%</td>
</tr>
<tr>
<td>Cu</td>
<td>8.19%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100%</strong></td>
</tr>
</tbody>
</table>

From the elemental weight percentage analysis it can be observed that there is a dominant quantity of oxygen present in the sample, which is justified as both alumina and CTO have a high stoichiometric ratio of oxygen in them. The weight presence of Ti and Cu along with Al indicates the presence of aluminum, titanium and copper in respective stoichiometric ratios.

To study the distribution of CTO nanoparticles onto alumina support, EDS mapping is performed. Fig. 4.18 shows the EDS mapping image of CTO nanoparticle immobilized alumina support. The image gives the distribution of aluminum (Al) represented as Al-K, titanium (Ti) represented as Ti-K, copper (Cu) represented as Cu-K and oxygen (O) represented as O-K in the image. From the image it is evident that the elements are distributed uniformly all over the surface of the support.
Fig. 4.19 presents the FESEM analysis performed to study the surface morphology of NTO nanoparticle coated alumina support. From the image it is observed that the surface of the support is highly porous in nature. The surface looks rigid and asymmetric patterns of pores are observed. The average diameter of these porous structures is in the order of 5 – 12 μm. EDS analysis is performed to study the elements present on the support surface. The EDS plot of alumina support immobilized with NTO nanoparticles is given in fig. 4.20. Table 4.5 gives the elemental weight percentage from EDS analysis.
Figure 4.19: FESEM image of NTO nanoparticles immobilized alumina support

Figure 4.20: EDS analysis of alumina impregnated with NTO
Table 4.5: Elemental weight % report of clay support impregnated with NTO nanoparticles

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>44.24%</td>
</tr>
<tr>
<td>Al</td>
<td>27.95%</td>
</tr>
<tr>
<td>Ti</td>
<td>15.19%</td>
</tr>
<tr>
<td>Ni</td>
<td>12.62%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100%</strong></td>
</tr>
</tbody>
</table>

From the elemental weight percentage analysis it can be observed that there is a dominant quantity of oxygen present in the sample, which is justified as both alumina and NTO have a high stoichiometric ratio of oxygen in them. The weight presence of Ti and Ni along with Al indicates the presence of aluminum, titanium and nickel in respective stoichiometric ratios.

To study the distribution of NTO nanoparticles onto alumina support, EDS mapping is performed. Fig. 4.21 shows the EDS mapping image of NTO nanoparticle immobilized alumina support. The image gives the distribution of aluminum (Al) represented as Al-K, titanium (Ti) represented as Ti-K, oxygen (O) represented as O-K and nickel (Ni) represented as Ni-K in the image. From the image it is evident that the elements are distributed uniformly all over the surface of the support.
4.5. Conclusion

Stable polymer support membranes are fabricated using PSf as the base polymer and PVP as a pore former. Membranes of varying concentrations have been fabricated and 15% PSf membrane was chosen for further experiments as the pore size of this concentration falls in the range of 85 – 100 nm.

Several techniques have been employed to immobilize Fe-Ni nanoparticles onto these 15% PSf membranes. It is observed from FESEM results that in-situ immobilization technique gave high porosity and pore volume that is suitable for the immobilization of nanoparticles. The membranes are found to have a specific surface area of 22.85 m$^2$/g and from the ICPMS analysis it has been noted that there is no leaching of Fe-Ni nanoparticles form the PSF membrane.
Ceramic supports based on alumina have been fabricated. The supports are found to be highly crystalline, mesoporous in nature and the specific surface area of these supports is found to be 95.14 m²/g. From the evacuation method of porosity measurement it is observed that the supports have an apparent porosity of 43%. NTO, CTO and FMO nanoparticles are immobilized onto these ceramic supports and from EDS mapping analysis it has been found that the distribution of nanoparticles is uniform all over the surface.