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Hossein Mahdavi* and Faeze Fayyazi

Preparation and Application of Palladium Nanoparticle Impregnated Chloromethylated Polysulfone Matrix as an Efficient Catalytic Membrane for Oxidation of Alcohols

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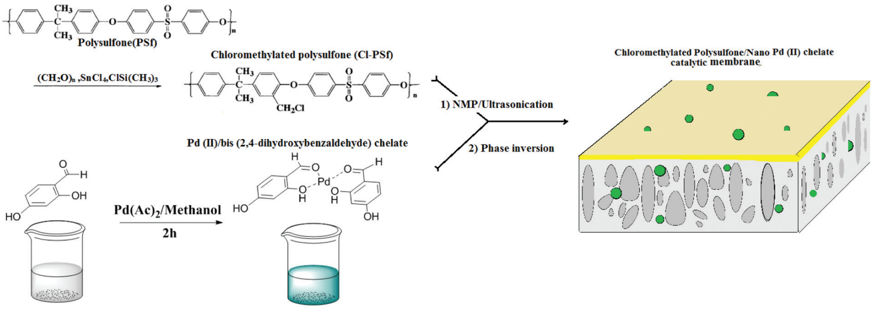
Abstract: The use of palladium nanoparticles embedded in a chloromethylated Polysulfone (CMPSf) matrix was developed for highly efficient oxidation of primary and secondary alcohols to corresponding aldehyde and ketone in organic solvent free condition. Pd (Π)/bis (2, 4-dihydroxybenzaldehyde) chelate chemically incorporated onto CMPSf was used to prepare beneficial catalytic membranes. Chemical structure and thermal properties of resulting membranes were characterized via FTIR, ^{1}HNMR, UV-vis, TGA and DSC techniques. Morphology and particle distribution throughout the catalytic membranes was elucidated using FE-SEM. An average particle size of Pd nanoparticles was estimated about 20 nm by XRD technique. ICP technique proved that no Pd particles were leached out of the membrane into the solutions; hence the as-prepared catalytic membranes could be used several times without significant loss in their activities. This is in good accordance with formation of chemical bond between Pd and polymer matrix.



***Corresponding author: Hossein Mahdavi,** School of Chemistry, College of Science, University of Tehran, P.O. Box 14155–6455, Tehran, Iran, Tel./Fax: +98–21–66495291, e-mail: hmahdavi@khayam.ut.ac.ir
Faeze Fayyazi: School of Chemistry, College of Science, University of Tehran, P.O. Box 14155–6455, Tehran, Iran

Keywords: catalytic membrane; oxidation of alcohols; Pd nanoparticles; polysulfone.

1 Introduction

The oxidation of alcohols to their corresponding aldehydes or ketones is an important reaction for both organic synthesis and industrial manufacture of fine chemicals such as dyes, medicines, agrochemicals and perfumes [1–4]. Traditionally performing such transformations have been involved with the use of stoichiometric or more than stoichiometric amounts of chromium (VI) salts or other metal oxidants. These reagents generate high quantities of hazardous waste of heavy metals and accomplish the oxidation reactions in solvents such as chlorinated hydrocarbons, which make them environmentally inappropriate. From an industrial perspective, heavy metal waste and solvent consumption led to the use of alternative processes such as transition metal catalysts with more moderate oxidants like H_2O_2, O_2 and air [5, 6].

Among the transition metal catalysts, palladium catalysts are capable of carrying out many chemical reactions such as cross-coupling, hydrogenation and oxidation reactions [7–14]. The common problem of the homogeneous catalysis system is squiring the reactions with missing of valuable metal complexes [6, 15, 16]. Many researchers have tried to solve this problem by offering various catalytic systems. Using catalytic membranes which are prepared from the incorporation of catalysts into polymeric membrane was one of the solutions offered by researchers. In this way the simultaneous product separation and reaction accompany with maintaining the catalyst and its catalytic activity will be possible [17–21].

Large diversity of polymeric materials with promising advantages such as facile film forming, low cost, solvent resistance and selective transformation of chemical species are suited for being used as catalytic membranes [22–26]. Among the various polymeric membranes, polysulfone (PSf) due to its good mechanical strength and stability at high temperatures has high popularity in membrane industry [27, 28]. In spite of its merits, PSf membranes suffer from fouling in filtration processes because of their intrinsic hydrophobic property [27–30]. Modification of PSf in order to increase its hydrophilicity can reduce this problem [31]. Furthermore, during chemical modification, it is possible to increase the reactivity of the main chain by introducing new reactive functional groups that permit further chemical reactions. Hence, a great deal of reports had been focused on the PSf modification. One of these modifications is chloromethylation, which can be performed under simple reaction conditions. This type of modification creates functional groups and creates possibility of chemical attachment between metal catalysts and polymer chains. Consequently, uniform distribution of the nano-palladium particles throughout the membrane takes place [31–35].

In this work we attempt to prepare and characterize a modified PSf membrane containing Pd chelate as catalyst and considering its catalytic activity for the oxidation of alcohols.

2 Materials and methods

2.1 Materials

PSf (MW 28000), chlorotrimethylsilane were purchased from Sigma Aldrich. 2,4-dihydroxybenzaldehyde, methanol (MeOH, bp 65 °C, >99.99%), 1-butanol (BuOH, bp 118 °C, >99.99%), 2-Propanol (PrOH, bp 97 °C, >99.7%), *N*-methyl-2-pyrrolidone (NMP), paraformaldehyde and chloroform were all purchased from Merck Company. All reagents were used without further purification except PSf, which was kept in a vacuum oven for 24 h before use.

2.2 Chloromethylation of PSf

Preparation of Chlromethylated PSf (CMPSf) was carried out by following the same method reported by Cozan and co-workers [35]. The polymer powder was kept in a vacuum oven at 50 °C for 24 h in order to remove moisture before using. PSf (3 g, 6.72 mmol) dissolved in chloroform (125 mL) into a flask equipped with stirrer and reflux condenser. Then paraformaldehyde (2 g, 67.2 mmol), trichloromethylsilane (8.5 mL) and tin (IV) chloride (12 mL) were added to the solution. The mixture was heated at 40–45 °C for 3 days. Then the solution mixture was poured into methanol under stirring. Finally, the precipitate was filtered and washed with methanol and finally dried in the vacuum at 40 °C for 18 h. The degree of PSf chloromethylation was estimated using Mohr’s titration method and was to be 12 mmol/g.

2.3 Synthesis of Pd chelate

In this study palladium chelate was synthesized according to the method of preparing Copper (II) bis(2,4-dihydroxylbenzaldehyde) [35]. 2,4-dihydroxybenzaldehyde (27.6 g, 0.2 mol) was dissolved in of methanol (100 mL). Then, Pd (II) acetate (0.3 g, 1 mmol) dissolved in of methanol (100 mL), and the stock solution was added very slowly to the above solution and kept stirring for

2 h, and finally allowed to cool in water bath at 0 °C. The resulting green solid filtered and washed with methanol and dried under vacuum at 60 °C for 18 h.

2.4 Immobilization of palladium chelate on CMPSf

CMPSf was dissolved in NMP to make 20 wt% polymer solutions. Desired amount of Pd chelate (10, 5, 2.5 mg) was added to solution of CMPSf (5 g) in NMP (2.5 mL). Later the solutions treated for 12 min under ultrasonic irradiation. Then they were kept under stirring for 5 h at room temperature and preserved under air tight condition for preparation of the nanocomposite membranes.

2.5 Preparation of membrane

The prepared solutions from previous step were cast using a Doctor Blade with thickness near of 200 µm. Then, the plate was immediately immersed in a distilled water bath for 1 min. The formed PSf-Pd membranes were washed with deionized water carefully to remove the residual solvent completely. The chemical metal reduction was accomplished with immersing the membranes into 0.1 M aqueous $NaBH_4$ solution.

2.6 Membrane performance study

To measure water permeability of the membranes, they were placed into the measuring cell where 25 mL of deionized water was poured into and the pressure of 1.5 bars was applied. The water flux was calculated according to the following equation:

$$\mathrm{J_w}(Lm^{-2}h^{-1}) = \frac{\text{Permeate volume}}{\text{Membrane surface area} \times \text{Filtration time}}$$

Membrane water uptake was determined by a simple method. Membrane samples were immersed in water for 48 h and weighed (W_w), then dried in the oven for 48 h at 80 °C and weighed again (W_d). Water uptake was calculated according to following equation:

$$\text{Water uptake}\,\% = [(W_w - W_d)/W_w] \times 100$$

Alcohols (5 mL) were fed in 4 cycles without washing between the steps. Membranes with the effective area of 3.14 cm^2 were placed in the home-made cell.

At this stage, the reusability of the catalytic membrane have been investigated. The reusability feature was studied fifty times for the alcohol oxidation.

At the end of each 10 cycles, the catalytic membrane was easily removed from the home-made cell and then washed with deionized water, and fresh alcohols poured in the home-made reactor to repeat the alcohol oxidation, and the results were collected.

Finally, we studied the leaching of PSf-Pd at the recycle experiments by determination of the Pd content in the extraction solution at the end of the reaction following a procedure using ICP-MS method its detection limits was <0.001 ppb.

2.7 Membrane performance

The alcohol oxidation reaction was carried out using glass homemade reactor as shown on Figure 1. The effective area of 3.14 cm^2 was connected in the inner core part of the reactor using connectors. The alcohol was fed through the part the pressure gauge installed. The gas was imported the reagents inlet section and cause both oxidation of alcohol and diffusion of the products from the inside to the outside of section. The temperature of the reactor was controlled through in-built electrical coil and it was monitored using a thermocouple. Reaction was carried out at a pressure of 1.5 bar and flux remained almost unchanged (1 mL/cm^2 s).

2.8 Characterizations

Transmission ATR-FTIR measurements were performed in KBr pellets with EQUINOX 55 Bruker FTIR specterometer. The ^{1}HNMR spectra were recorded on a Bruker Avance 500 MHz spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard (a reference). The scanning electron microscope images were taken with Hitachi S-4160 electron microscopy. Differential scanning calorimetry (DSC) measurements were done using a Q 100790 Build 275 instrument DSC

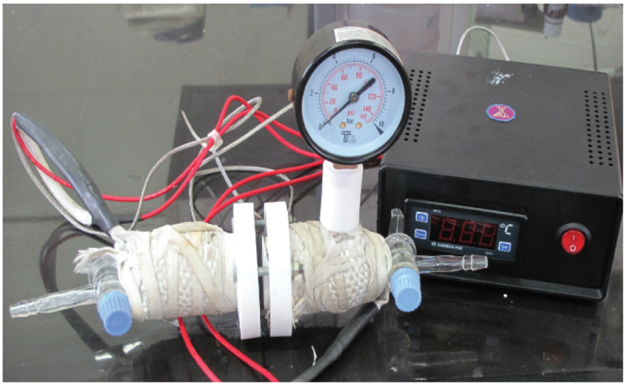


Fig. 1: Homemade cataytic membrane system cell.

with a heating rate of 20 °C/min. The temperature range was between 25 and 250 °C. Thermo gravimetric analysis (TGA) was carried out using a Q 50 (TA, USA) instrument over the temperature ranging 30 °C–800 °C at a heating rate of 10 °C/min under a nitrogen stream. X-ray measurements were performed with a X-pert Philips Co Kα radiation (40 kV, 40 Ma, $\lambda = 1.54051A0$) instrument over a 2θ range from 20° to 100°. UV-vis absorption spectra were collected by UV Perkin Elmer spectrometer. Gas chromatography (GC) analyses were done on Shimadzu gas chromatograph instrument. A Varian Spectra A-400 atomic absorption spectrometer equipped with a deuterium background correction and an air–acetylene burner was used for the analysis.

FTIR (EQUINOX 55 Bruker) spectroscopy was applied for verification of oxidation of alcohols. The yields of the products were analyzed using GC Shimadzu gas chromatograph instrument. Chemical analyses (ICP: Varian VISTA- MPX) was carried out after oxidation reaction in order to estimate the amount of palladium washed from the membrane. The film catalysts were characterized by DSC (Q 100790 Build 275), XRD (X-pertPhilips, pw 3040/60), SEM (Hitachi S-4160), and UV-visible (Perkin Flmer) instruments.

3 Results and discussions

3.1 Analysis and evaluation of chlromethylated polysulfone

Chloromethylationprocess of the polysulfone polymer was confirmed qualitatively by FTIR (Figure 2). The results indicated clearly the presence of methylene

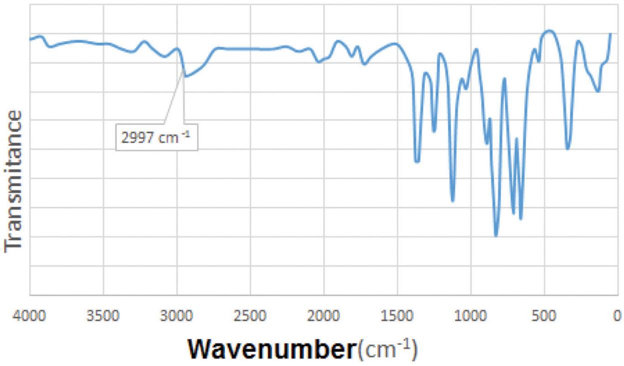


Fig. 2: FTIR spectra of CMPSF.

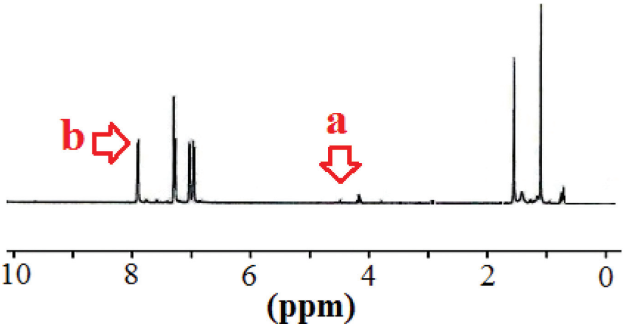


Fig. 3: ^{1}HNMR spectra of chloromethylated PSf.

groups along the polymer backbone after chloromethylationreaction carried out. This can be observed at 2993 cm^{-1} in FTIR spectrum, which is related to the stretching of the methylene (CH_2) groups.

The contents of chlorine ion, was determined by potentiometric titration, with 0.05 N $AgNO_3$ aqueous solutions. The degree of substitution for the modified PSf was estimated 6%.

The percent of chloromethylation per repeat unit (DS, degree of substitution) was determined from the integrated intensity of proton peak at 4.56 ppm in the ^{1}HNMR spectrum [denoted in Figure 3 as (a)], relative to that of the reference peak at 8.0 ppm, which represents the four meta protons on the phenyl ring closest to the sulfonyl group [denoted in Figure 3 as (b)].

3.2 Thermal gravimetric analyses

The thermal stability of the polymer membranes was studied by thermal gravimetric analysis (TGA). The TGA curve Figure 4 shows a weight loss in the temperature range from 243 to 290 °C, corresponding to the loss of water and solvent molecules. The content of water and solvent was calculated about 19.7%. The residual solvent could only be removed well above its boiling point when the polymer is in the rubbery state. A weight loss about 11.46% starts at 374 °C is attributed to the loss of chloromethyl groups. The third weight loss of CMPSf sample is observed at 480.96 °C corresponding to the polymeric backbone degradation. It was observed that the decomposition temperature of the polymer main chain decreased by chlromethylation. These differences could be explained by a reduction symmetry in the polysulfone structure due to the introduction of CH_2Cl groups renders it less regular and therefore, less stable.

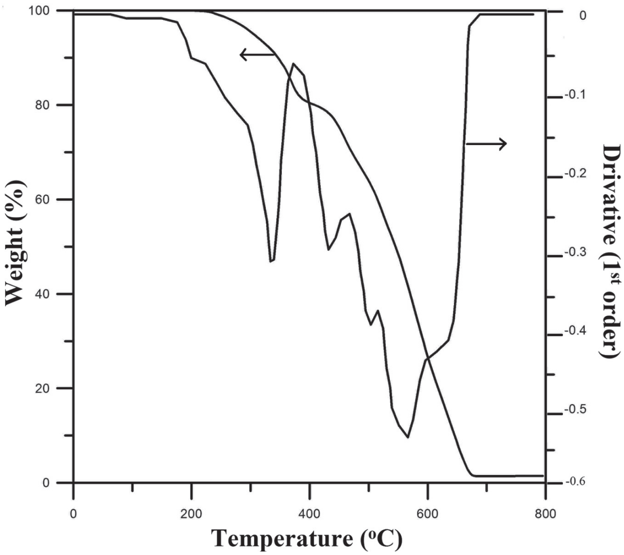


Fig. 4: TGA diagram of chloromethylated PSF.

The degree of chloromethylation of PSf was estimated about 12%, 11.47% and 6% by ^{1}HNMR, TGA and Mohr's titration, respectively. As seen the value obtained by titration is not in agreement with that of other two methods. This is attributed to the fact that the all chloromethylene groups on PSf are not accessible and missing of some chloromethylene groups in titration because of slow segmental motion of PSf chains. Hence, the obtained titrated value will be deviated from the actual amount.

3.3 Palladium chelate analyses

Formation of complex confirmed qualitatively by FTIR technique. Clearly, presence of the aldehyde group (CHO) was confirmed by absorption peak at 1660 cm^{-1} (Figure 5). In addition, UV-Vis spectra of Pd chelate shows two sharp peaks (Figure 6) which are attributed to transition of the benzenoid ring $\Pi \rightarrow \Pi^*$ (282 nm) and oxygen non-bonding electron pairs $n \rightarrow \Pi^*$ (340 nm).

3.4 CMPSf membrane containing palladium chelate analyses

UV-vis spectroscopy was performed to verify the incorporation of modified PSf with Pd chelate. Significant differences between the UV-vis spectra of the PSf and

PSf containing Pd chelate were observed, which are shown in Figure 7. An absorption peaks at 285 nm appeared in the spectra of the PSf, this peak is assigned to the $\pi \rightarrow \pi^*$ transition of the benzenoid ring. On the other hand, in the UV-vis spectrum of PSf containing chelate of palladium, this peak was shifted to 265 nm indicating the hypsochromic effect due to the non-hybrid electron pairs of oxygen.

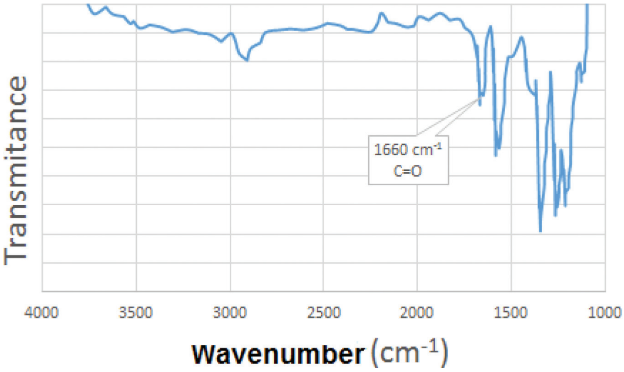


Fig. 5: FTIR spectra of palladium chelate.

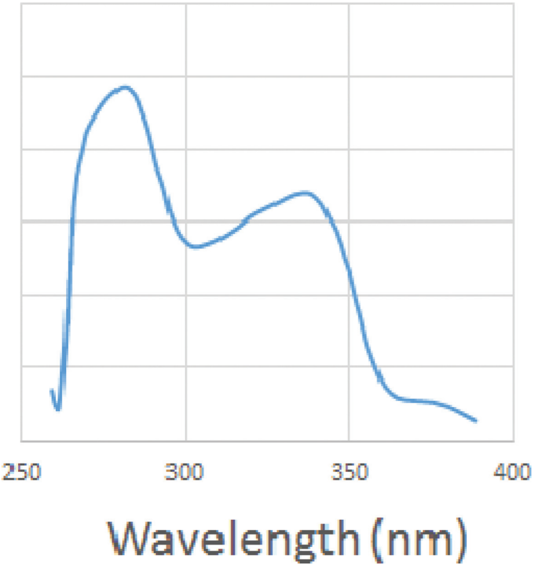


Fig. 6: UV-vis absorption spectra of palladium chelate.

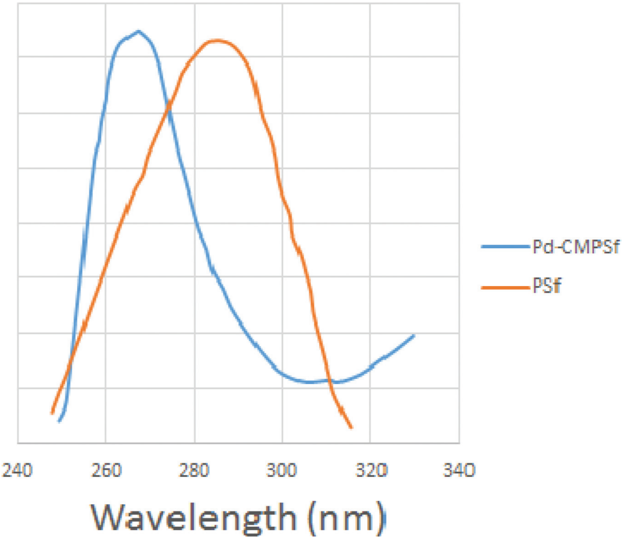


Fig. 7: UV-vis absorption spectra of PSf and CMPSf containing palladium chelate.

In order to calculate the amount of palladium chelate atomic absorption analysis was used. The amount of palladium per gram of Polysulfone was to be about 20.7 ppm. The X-ray diffraction pattern of the catalytic membrane powder is shown in Figure 8.

The Bragg reflection peaks at 2Θ equals to 40° and 67° are attributed to diffraction from the planes of (1,1,1) and (2,2,0) Average Pd particle size of 20 nm was estimated by the Debye Scherrer formula from XRD pattern.

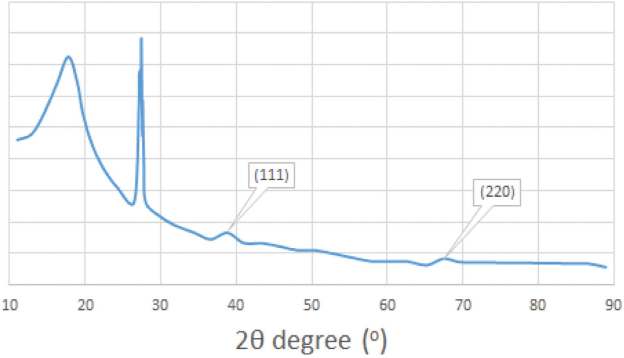


Fig. 8: XRD pattern of PSf membrane containing 1% Pd chelate.

3.5 Differential scanning calorimetery study of prepared PSf-Pd membrane

Differential scanning calorimeter provides useful information about polymer thermal behavior and transitions. Chemical structure of polymer chains and interactions among them has significant effect on T_g. Some of the factors could decrease the glass transition temperature by reducing interaction between polymer chains and increasing distance between chains. For example forming functional groups on the polymer chain will cause decrease of T_g by making their mobility easier. Considering that the glass transition temperature of polysulfone is 188 °C, the T_g of polysulfone containing palladium nanoparticles was reduced about 14 °C compared to the bare PSf (Figure 9). It is possible to consider that palladium chelated nano particles cause to create distance between chains, and this makes movements of PSf chains easier. The decrease in T_g of PSf after blending with Pd chelate means that there is a certain interaction or bonding between the two materials.

3.6 Morphological studies

SEM micrographs were used to investigate surface morphology of catalytic membranes. The SEM images of the three membranes were prepared with different percents of Pd chelate are shown in Figure 10. No significant aggregations were found. However, as the Pd chelate content increased, the aggregation of Pd chelate slowed down.

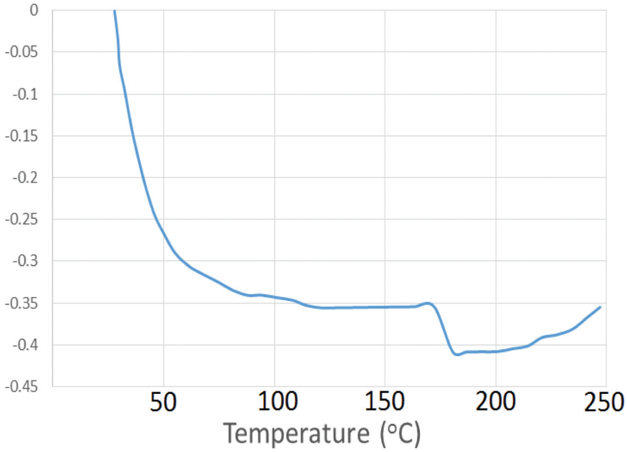


Fig. 9: DCS diagram of chemically modified PSf membrane containing 1% Pd chelate.

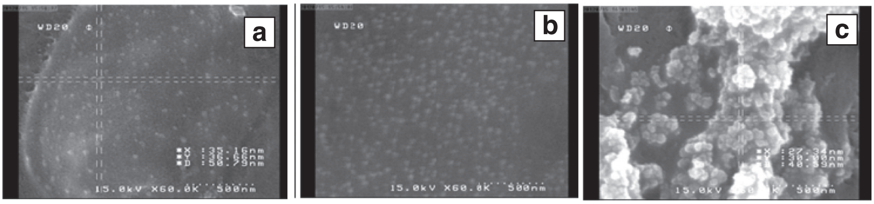


Fig. 10: SEM micrographs of catalytic membranes surface containing (a) 0.5%, (b) 1% and (c) 2% Pd chelate *Catalytic oxidation of alcohols*.

Tab. 1: Comparison data of the aliphatic alcohol oxidation.

Entry	Alcohol	Presence of pure oxygen (Yield %)	Presence of air (Yield %)
1	Methanol	40	30
2	2-Propanol	70	40
3	1-butanol	60	35

The poured alcohol in the home-made cell was transported through the membranes containing 1% nanoparticles and transformed to the desired products simultaneously without using bases or solvents. With this method, the obtained products will have more purity, and since it could be separated during the reaction. Reaction was carried out at a pressure of 1.5 bar and flux remained almost unchanged (1 mL/cm^2 s).

Aliphatic alcohols in four cycles passing through the membrane at 30 °C were oxidized in the presence of pure oxygen and air (Table 1). The obtained yield in the presence of pure oxygen is significantly higher than presence of air.

3.7 Reusability of catalytic membrane

The reusability of catalytic membrane is a very significant theme and makes them useful for commercial applications. The prepared catalytic membrane showed high stability of the catalyst activity in the oxidation reactions.

In the alcohol oxidation reaction, Pursuant to table data (Table 2) it is seen that lower decrease in activity (7%) for catalytic membrane compared to 73% decrease for PSf membrane after fifty cycles. The high yields of oxidation products and almost constant activity over up to 50 reaction cycles, indicate the outstanding reusability of the catalytic membrane in the alcohol oxidation reaction. On the other hand, ICP analyses proved the absence of significant catalyst leaching into the permeate solution.

Tab. 2: The reusability of catalytic membrane.

Number of cycles	10	20	30	40	50
Yield %	73	70	68	68	66

4 Conclusions

Well-dispersed PSf-Pd chelate nanocomposite was synthesized through a facile method and then used as the catalytic membrane. In summary, we have developed an efficient and simple procedure for selective oxidation of organic compounds, using an eco-friendly catalytic system consisting of Pd chelate catalyst. Most importantly, this catalytic membrane could be reused in further fifty time's reactions without any significant loss of catalytic activity and nanocomposite catalytic membrane has a great potential for industrial production and practical application.

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