



Mixed metal nanoparticles loaded catalytic polymer membrane for solvent free selective oxidation of benzyl alcohol to benzaldehyde in a reactor

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ABSTRACT

Catalytic polymer membrane (CPM) was prepared by *in situ* loading of mixed (silver and lead) metal nanoparticles (MNPs) in sulfonated poly(ether sulfone) (SPES) matrix. Developed membrane (SPES-Ag⁰(35)/Pb⁰(65)) was used as a catalyst (oxidant) loaded and separator, in two-compartment catalytic membrane reactor (CMR) for selective oxidation of benzyl alcohol (BnOH) to benzaldehyde (BzH) in ambient conditions without regeneration of catalysts, separation steps and waste generation. CPM acts as barrier and contactor between organic and aqueous phase, which was characterized by FTIR, XRD EDX, SEM, and physicochemical properties. Reported SPES-Ag⁰(35)/Pb⁰(65) showed good solvent, chemical and thermal stabilities in compare with fluorinated membrane and assessed to be more suitable for CMR. Effects of various reaction parameters such as substituted BnOH, concentration, silver nanoparticles (AgNPs) load *etc.* were investigated. High performance, low cost and stability of reported SPES-Ag⁰(35)/Pb⁰(65) suggested its commercial viability for chemical transformations in CMR.

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1. Introduction

Generally, oxidation of hydrocarbons has been achieved by heavy metal reagents and toxic solvents, which generates hazardous waste. Based on principle of green chemistry, selective oxidation of hydrocarbons is an important chemical transformation. Aldehydes and ketones are essential chemicals, synthesized by oxidation of alcohols in presence of volatile organic solvents using stoichiometric inorganic oxidants, and chromium reagents [1–4]. From point view of green chemistry, there is an exigent demand for efficient, cost-effective and environmentally benign process for synthesis of aldehydes and ketones, which avoids catalyst recycling, clean oxidants such as O₂ [1,5–10].

CMR offers many practical advantages and considered as an innovative device for achieve the chemical transformations with high selectivity, without any additional costs of separation of by-products and waste generations. CMR with hydrophobic/hydrophilic CPMs were highly desirable during catalytic chemical and biochemical reactions [11–15]. To enhance the interfacial area of metal catalysts in CPMs, immobilization of metal nanoparticles (MNPs) attracted increasing attentions due to high percentage of surface atoms and the associated quantum effects [16,17]. To avoid the MNPs aggregation and enhance their stabilization without any catalyst loss or recovery, incorporation of MNPs

in polymer matrix offers unique possibilities for enhanced access of reactants to the catalytic sites [18,19]. *In situ* synthesis of MNPs into a polymer matrix permits synergised catalytic activity, without any destruction and pollutants separation [20,21]. Thus, CPMs should consists of stable (chemical, thermal, and mechanical), and processable polymer matrix [22].

Numerous polymeric membranes such as PVDF [23,24], PTFE [25], alumina [26], lead Nafion[®] 417 coated ruthenate pyrochlore [27], PDMS/PVA [11], Fenton coated Nafion [28] and ceramics [29], were used in CMR, because of their excellent stabilities in harassed conditions [17–19]. But, hydrophilic/hydrophobic modifications of these polymeric membranes are difficult. As an alternate, poly(ether sulfone) (PES) were successfully proposed as cost effective, fluorine-free polymer [30–32]. PES is a moderate oxidative, solvent resistance and stable (mechanical, chemical and thermal) polymer, because of aromatic rings and strong chemical bonding between carbon, sulfur and oxygen [32–35]. Further, functionalization (sulfonation) of PES provides acidic membrane matrix, suitable for loading of metal ions by ion-exchange and further metal ions reduced by strong reducing agent to MNPs formation. This novel approach for developing MNPs loaded CPMs completely ruled out the leaching of catalytic active centre. Thus, suitability of MNPs loaded SPES membrane has explored as CPM (SPES-Ag⁰(35)/Pb⁰(65)) for selective oxidation of benzyl alcohol (BnOH) to benzaldehyde (BzH) in a CMR.

Selective oxidation of BnOH to BzH is of industrial importance, use of latter in cosmetics and flavour industries, in which presence of impurities (organic chlorine or benzoic acid) is a serious

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concern [36,37]. Furthermore, the present route does not conform the guidelines of green chemistry (zero discharge, maximum atom utilization efficiency, avoid the use of solvents, and catalysts) [15]. High performance catalysts with low temperature activity/selectivity are also challenge. Silver based catalysts including electrolytic silver catalyst has been reported for gas phase selective oxidation of BnOH to BzH [38]. But electrolytic silver is not active below 500 °C and not selective above 500 °C because of cracking and over oxidation [38]. Recently supported silver catalyst on Ni-fibers has been demonstrated for gas phase selective oxidation of BnOH to BzH with 91% conversion and about 85% selectivity at 380 °C [10]. Latter on same research group also proposed Ag/Ni fiber catalysts for the selective oxidation of BnOH at 120 °C. But regeneration of catalysts, separation of un-reacted reactants and products and reaction at elevated temperature, are unsolved limitations.

Herein, we are reporting highly selective and stable CPMs loaded with MNPs (Ag^0 and Pb^0) in the acidic functionalized SPES matrix for selective oxidation of BnOH to BzH without any by-product or waste generation and separation steps in a CMR. Reported process showed selective oxidation at the interface of CPM, and due to low permeation of BzH across the CPM to aqueous phase, its over-oxidation was protected.

2. Experimental

2.1. Materials

PES (Udel P-3500) was received from Solvay Advanced Polymers. Benzyl alcohol (BnOH), p-anisyl alcohol, m-nitro benzyl alcohol, methanol, toluene, silver nitrate, lead nitrate, hydrazine hydrate of AR grade, were obtained from S.d fine Chemicals, India. All chemicals were used without any further purification. Double distilled water was used for all experiments.

2.2. Preparation of catalytic polymeric membrane

Detailed procedures for sulfonation of PES and preparation of SPES membranes have been described (Section S1, Supporting informations) [34]. SPES membranes were conditioned in HCl and NaOH solutions (0.10 M) alternatively, and washed with distilled water. Procedures for estimation of water content, ion-exchange capacity (IEC), membrane tortuosity (τ) and porosity (ϵ) are included (Section S2, Supporting informations). Physicochemical and electrochemical properties of SPES membranes are included in Table S1 (Supporting informations). Thickness of the membrane was measured as average values of three consecutive measurements with digital micrometer (1.0 μm sensitivity).

Fig. 1 shows the typical preparation methodology for the catalytic polymeric membrane (CPM). A piece of SPES membrane (25 cm^2) was equilibrated with mixed solution (35 mM AgNO_3 and 65 mM PbNO_3) to allow the exchange of H^+ with Ag^+ or Pb^{2+} for 24 h. After careful washing with deionised water, membrane was immersed in hydrazine hydrate (1.75 wt%) at 50 °C for 24 h, to reduce the metal ions into metal nanoparticles (MNPs). Three CPMs (SPES- $\text{Ag}^0(35)/\text{Pb}^0(65)$; SPES- $\text{Ag}^0(50)/\text{Pb}^0(65)$ and SPES- $\text{Ag}^0(65)/\text{Pb}^0(65)$) were prepared in which loading Pb^0 NPs was constant (65 mM PbNO_3) while loading of Ag^0 NPs was varied (35–65 mM AgNO_3) in the SPES matrix.

Uniform distribution of MNPs (catalytic active sites) on the membrane surface was confirmed by SEM images. Loading of MNPs in the membrane phase was obtained from weight difference method and varied between 60 and 75 mg/g (0.25–0.40 mmol of metal ions per gram of dry weight membrane). Photo images of the SPES and SPES- $\text{Ag}^0(35)/\text{Pb}^0(65)$ membranes are depicted in Fig. S1 (Supporting informations), which also confirmed loading of MNPs in the SPES matrix.

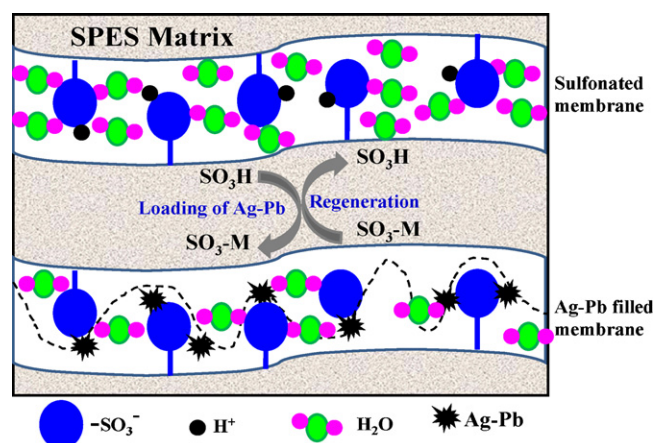


Fig. 1. Schematic presentation of CPM used in CMR.

2.3. Mass transport model

When reactants contact by diffusion across the SPES- $\text{Ag}^0(35-65)/\text{Pb}^0(65)$ matrix, the chemical conversion strongly influenced by the catalytic performance of diffusing medium (Fig. S2, Supporting informations). For best performance, mass transfer resistance should be low with limited reaction regime. Prepared SPES- $\text{Ag}^0(35-65)/\text{Pb}^0(65)$ membranes were nanoporous with 29–20% overall porosity (ϵ) (Table 1). Diffusivity (D_{eff}) across SPES- $\text{Ag}^0(35-65)/\text{Pb}^0(65)$ membrane differs from the bulk (D_0) and its values can be determined by overall porosity (ϵ), and tortuosity (τ), which revealed the membrane porous structure and steric hindrance:

$$D_{eff} = \frac{D_0 \epsilon}{\tau \theta} \quad (1)$$

where,

$$\theta = \left[\frac{r_p - r_s}{r_p} \right]^4 \quad (2)$$

r_p is mean radius of the pore, while r_s 'Stokes radius of the reagent' can be obtained by [23].

$$r_s = \frac{\kappa_B T}{6\pi\eta D} \quad (3)$$

κ_B is the Boltzmann constant (JK^{-1}), D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), η viscosity of solution and T is the absolute temperature.

2.4. Instrumental analysis and membrane stabilities

Detailed instrumental analysis have been included in the section S3 (supporting informations). Oxidative stability of SPES- $\text{Ag}^0(35-65)/\text{Pb}^0(65)$ membranes was evaluated in Fenton's reagent (3% H_2O_2 aqueous solution containing 3 ppm FeSO_4) at 80 °C for 1 h. For the hydrolytic stability test, a small piece of membrane (30 mm) was boiled in water for 24 h at 100 °C in a pressurized closed vial. Membrane stability was evaluated in turns of weight loss and the physical appearance of the test samples. Chlorine stability tests were assessed in 5% NaOCl aqueous solution at 80 °C for different

Table 1
Physicochemical properties for SPES and different CPMs membranes.

Membrane	φ_w (%)	t (μm)	τ	θ	ϵ	ϵ/τ
SPES	13.7	150	0.93	0.34	0.39	0.42
SPES- $\text{Ag}^0(35)/\text{Pb}^0(65)$	5.80	127	0.85	0.29	0.22	0.25
SPES- $\text{Ag}^0(50)/\text{Pb}^0(65)$	4.10	135	0.80	0.24	0.29	0.36
SPES- $\text{Ag}^0(65)/\text{Pb}^0(65)$	2.89	137	0.74	0.25	0.20	0.27

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