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Development of Functional Catalyst System for Hydrogen Production from the Hydrolysis of Chemical Borohydride

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Abstract: *Nanocomposites and porous materials have gained much attention and have tremendous potential over the homogeneous catalysts.Microporous organic polymers can serve as a special material for incorporating nanoparticles or ionic liquids, which can allow the material for wide potential applications in gas storage, gas separation, hydrogen production and catalysis. The hypercross-linked polymeric ionic liquid membranes used herein is particularly simple to prepare, since a commercially available polymer is used as a starting material and the polymeric ionic liquid networks is obtained solely by Friedel-Crafts alkylation reaction. The as-prepared hypercross-linked porous polymeric ionic liquid membranes were tested for hydrogen generation.*

Keywords: *ionic liquids, hypercross-linked organic polymers, high surface area, H_2 generation, $NaBH_4$*

1. INTRODUCTION

Higher energy costs due to need of fossil fuels and the related environmental issues have motivated the search for alternative, renewable fuel options. Hydrogen is one of the important energy carriers, because it produces no emissions at the point of use [1]. Numerous methods have been reported for hydrogen generation, such as coal gasification, biomass pyrolysis and gasification, electrolytic or photo catalytic water splitting and hydrolysis of chemical hydrides. Metal borohydrides such as lithium hydride (LiH), sodium aluminium hydride (NaAlH4), lithium borohydride (LiBH4), and sodium borohydride (NaBH4) have gained more attention as potential hydrogen storage materials due to their high hydrogen content. Among these hydrolysis of $NaBH_4$ is particularly attractive in view of its various advantages. It has a higher hydrogen content (10.8wt%) and its equivalent energy density is nearly equal to that of diesel fuel [2]. There are many catalysts such as platinum, palladium, $CoCl_2$, $NiCl_2$, Al_2O_3 have been studied for this reaction. However, they have some drawbacks such as low stability, recyclability issues, and expensive.Nanocomposites and porous materials have gained much attention and have tremendous potential over the homogeneous ones and through heterogenizing the catalyst certain practical limitations of the homogeneous system can be eliminated. The most promising advantages of nanocatalysts are easy separation from the reaction mixture, allowing recovery of the solid and eventually its reuse, provided that the recovered catalyst has not become deactivated during the course of the reaction [3]. In our group we have developed functional materials like electrospunnanofibers PVDF/ionic liquids (IL) nanocomposites [4], fabirication of IL/PVDF polymer networks [5], carbon nanotube/IL/Mnnanohybrids [6]. They have shown excellent performance for hydrogen generation from the hydrolysis of NaBH4. Due to the success of these materials, we have developed highly novel and porous materials using ionic liquids. Ionic liquids are salts and are composed solely of anions and cations. The main advantage of ionic liquids is that they are a new class of solvents by their non-molecular nature [7]. Microporous organic polymers (MOPs) can serve as a special material for incorporating nanoparticles or ionic liquids, which can allow the material for wide potential applications in gas storage, gas separation, hydrogen production and catalysis [8]. The hypercross-linked polymeric ionic liquid membranes used herein is particularly simple to prepare, since a commercially available polymer is used as a starting material and the polymeric ionic liquid networks is obtained solely by Friedel-Crafts alkylation reaction.

2. EXPERIMENTAL

2.1. GENERAL PROCEDURE FOR SYNTHESIS OF POROUS POLYMERIC IONIC LIQUID MEMBRANES

The polymeric ionic liquid solution used for preparing membrane as follows: 40 wt.% of polystyrene (PS) and 3 wt.% ionic liquid was added to 5 mL of dimethylformamide to obtain a homogenous solution. These solutions were placed on a glass substrate and drawn into a membrane using membrane casting knife. Then solvent was allowed to dry for appropriate time. The microporousorganic polymer networks were synthesized by Friedel-Crafts alkylation of PS/IL membranes, formaldehyde dimethylacetal (FDA) as a cross-linker, 1,2-dichloroethane as solvent and $FeCl_3$ as a catalyst was combined and stirred in an ice bath until completely mixed. PS/IL membranes were added to the mixture, and then the mixture was heated to 80 ºC for 24 h without stirring. The resulting membranes were washed with ethyl acetate, and then dried in a vacuum oven at 60 ºC.

3. RESULTS AND DISCUSSION

The synthesized hypercross-linked porous PS/IL membranes were characterized by SEM, EDX and FTIR. Figure 1 shows the SEM images of the membranes. The catalytic activity of the as-synthesized membranes for $NaBH_4$ hydrolysis was studied at room temperature. The self hydrolysis of $NaBH_4$ without catalyst or only the support PS membranes was negligible. The rate of hydrogen generation astonishingly increased when hypercross-linked porous PS/IL membranes were introduced into the $NaBH_4/H_2O$ system. This indicates that the IL successfully incorporated into the hypercross-linked porous PS membranes. To support this point, we have performed another reaction with same experimental conditions by using non-porous PS/IL membranes before cross-linking. As shown in Figure 2 both porous and non-porous PS/IL membranes demonstrated different catalytic activity. This is highlighting the dominant factor of hierarchical porosity and high surface area of the membranes. The higher catalytic activity can be attributed to structural characteristics of ionic liquid (which has both organic and inorganic ions) and porous PS membranes.

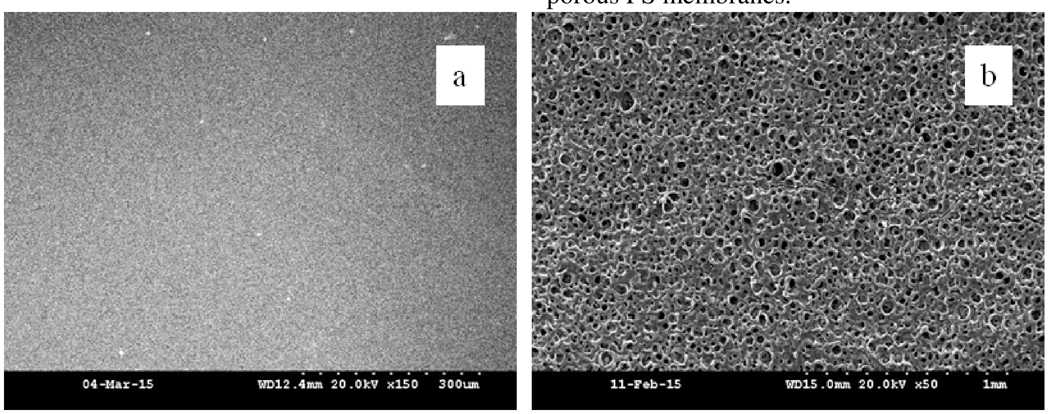

Fig.1. SEM image of (a) non-porous PS (b) hypercross-linked porous PS/IL membranes.

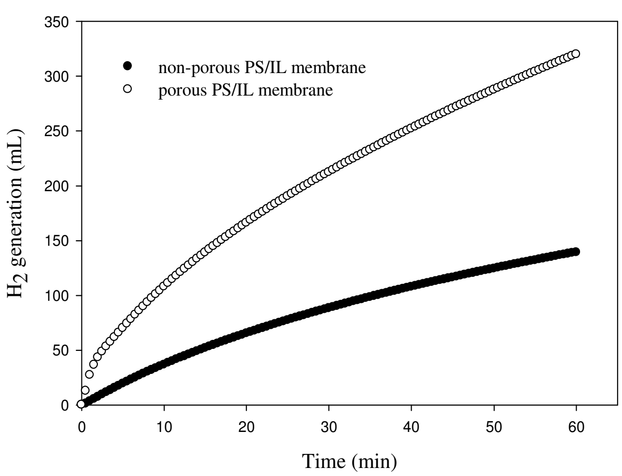

Fig. 2. Volume of H_2 versus time plots for the hydrolysis of 50 mL of 158.72 mM $NaBH_4$ catalyzed by non-porous and hypercross-linked porous PS/IL membranes at 30 ± 0.1 ºC.

4. CONCLUSIONS

In conclusion, the catalytic activity of hypercross-linked porous PS/IL membrane on hydrogen generation by hydrolysis of $NaBH_4$ was examined. There was a huge differences observed between porous and non-porous PS/IL membranes in terms of catalytic activity, this can be due to the nature of the supports and their related properties

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