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Nickel Sulfide Nanoparticles Incorporated Poly(methyl methacrylate)-Zirconia Membranes for Ultra Deep Desulfurization of Dibenzothiophene

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Abstract

Ultra deep desulfurization of liquid fuels such as gasoline/diesel has attracted considerable attention of modern clean fuel research due to strict environmental regulations. Apart from that, SO_x produced during combustion, poison the catalytic converter and exhaust emission system. Comparing to conventional catalytic and hydrodesulfurization techniques, adsorptive method for removal of sulfur bearing compounds e.g. thiophene derivatives is a promising approach which does not require hydrogen gas and high temperature. In this study, we used nickel sulfide nanoparticles incorporated poly(methyl methacrylate)-zirconia membranes as potential affinity material for adsorptive extraction of dibenzothiophene from n-hexane. The functionality and surface morphology of synthesized material was examined by Fourier transformation infrared (FTIR) spectroscopy and atomic force microscopy (AFM) images, respectively. The quantitative data regarding adsorptive removal of dibenzothiophene was determined by monitoring the shift in absorbance values of standard solutions before and after treating with synthesized material under ambient conditions. Nickel sulphide nanoparticles exhibited suitable rebinding response for removal of dibenzothiophene down to 1 ppm due to affinity interactions which is useful concerning ultra deep desulfurization. Finally, nickel sulphide nanoparticles were incorporated in poly(methyl methacrylate)-zirconia membrane which showed potential application for adsorptive desulfurization of dibenzothiophene at ambient conditions.

INTRODUCTION

During the last decade, significant efforts are made for developing renewable energy sources but nevertheless, fossil fuels still holds the importance as primarily source of energy to meet the requirements. Crude petroleum oil is a complex mixture that contains a variety of hydrocarbons along with various sulfur bearing compounds as contaminants. The presence of sulfur compounds in diesel or gasoline fuel has adverse effects on environment as it leads to SO_x emission and furthermore, it poisons the exhaust catalyst and reduces its activity considerably. Therefore, due to modern day environmental regulations and for improved performance of catalytic converter, it is highly imperative to remove sulfur compounds to produce clean fuels. Although the distillation refineries cut a major amount of sulfur compounds however, subsequent desulfurization [1] is still needed to reduce organo sulfur compounds from fuel.

Hydrodesulfurization [2-4] is an established industrial method that is used to remove sulfur containing compounds such as thiols, sulphides, mercaptans and others. In this process, sulfur compounds are reacted with hydrogen in the presence of bimetallic catalyst [5] e.g. NiMo above 300°C and high pressure. However, this method is not effective against thiophenes and their alkylated derivatives due to their reduced activity and thus, more rigorous conditions of higher temperature, pressure and hydrogen gas are required. It is also important to mention here that thiophene derivatives represent more than 50% of total sulfur compounds present in crude oil. Thus, the removal of thiophene compounds from diesel/gasoline fuels is challenging and demand alternative approaches.

Adsorptive desulfurization [6-8] is an efficient and low cost method for removing thiophene compounds from fuel. The highlight of this strategy is that it does not require severe conditions of temperature or pressure. In literature, there are number of potential adsorbents used for desulfurization applications including activated carbon [9], alumina [10], metal organic frameworks [11] and others. While developing such adsorbent, it is important to design a surface that possesses special affinity with thiophenes and can interact with them at ambient conditions [12]. Furthermore, high chemical stability is also desired keeping in view corrosive nature of crude oil.

Herein, we developed nickel sulphide nanoparticles incorporated poly(methyl methacrylate)-zirconia (PMMA-ZrO_2-NiS) membrane for adsorptive desulfurization of dibenzothiophene. Polymethyl methacrylate (PMMA) is used as base matrix of adsorption membrane while zirconia (ZrO_2) powder was added to ensure improved chemical and thermal stability to the matrix. Nickel sulphide (NiS) nanoparticles were used as potential affinity material for dibenzothiophene (DBT) recognition preferably at low ppm concentrations. The developed PMMA-ZrO_2-NiS membrane demonstrated suitable potential for adsorptive deep desulfurization of thiophenes at ambient conditions without using hydrogen or catalyst.

EXPERIMENTAL

Materials

All the chemicals and regents were used as received from supplier. Nickel sulphate hexahydrated ($NiSO_4.6H_2O$), zirconia powder (ZrO_2), dibenzothiophene ($C_{12}H_8S$) and polymethyl methacrylate -$(C_5H_8O_2)_n$- of avg. Mw ~ 350,000 were obtained from Sigma Aldrich. Sodium hydroxide (NaOH) and chloroform ($CHCl_3$) were used from Merck whereas thioacetamide (C_2H_5NS) was purchased from Uni-Chem.

Synthesis of NiS Nanoparticles and PMMA Membranes

NiS nanoparticles were synthesized by already established hydrothermal method. Here, 0.63 gm of nickel sulphate hexahydrated, 0.216 gm of thioacetamide and 0.144 gm of sodium hydroxide were dissolved in 80 mL distilled water. This mixture was transferred into Teflon lined stainless steel autoclave and heated at 160°C for 24 hours. After that the autoclave was cooled to room temperature and resultant black coloured NiS nanoparticles were separated by centrifugation. The collected nanoparticles were thoroughly washed with water and ethanol to remove reaction by-products.

A schematic representation of three different types of PMMA membranes has been depicted in figure 1. In the first case, plain PMMA membrane was developed by dissolving 1 gm of PMMA in 15 mL of chloroform and subjected to magnetic stirring for 30 minutes followed by another 30 minutes of ultra-sonication. This mixture was transferred to glass petridish and solvent was evaporated at room temperature. This leads to the formation of transparent PMMA membrane. In second case, 1 gm of PMMA was dissolved in 15 mL of chloroform under stirring and then 5 mg of ZrO_2 was dispersed in this solution and subjected to ultra-sonication for 30 minutes. This mixture was transferred to glass petridish and chloroform was evaporated to obtain PMMA-ZrO_2. In third case, 1 gm of PMMA was dissolved in 15 mL of chloroform and then, 5 mg of ZrO_2 and 10 mg of as-prepared NiS nanoparticles were added to this solution. This mixture was also processed in the same way as described above to have PMMA-ZrO_2-NiS.

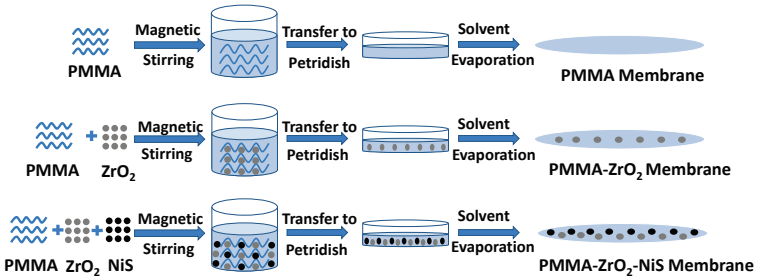

Figure 1: Schematic representation of PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS membrane formation.

Characterization

The synthesized PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS membranes were characterized by Agilent Cary 630 Fourier transformation infrared (FTIR) to observe structural functionality. The surface morphology of these membranes was investigated by Shimadzu SPM-9700HT atomic force microscope (AFM) images.

Rebinding tests

In rebinding tests, the as-prepared NiS nanoparticles were first tested for their recognition properties by exposing against standard solutions of DBT i.e. in the range of 1-5 ppm made in n-hexane at room temperature. UV/Vis absorbance values of these standard solutions were noted before and after treating with NiS nanoparticles. In the

next phase, the developed PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS membranes were tested against standard DBT solution and subsequent shift in absorbance was monitored.

RESULTS AND DISCUSSION

The PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS membranes were synthesized by solution casting method and their corresponding FTIR spectra are shown in figure 2 as follows. All three spectra look quite similar to each other as in all three cases the presence of CH_3 and CH_2 groups in PMMA chain are indicated by their stretching vibrations at 2951 cm^{-1}. A strong and intense peak around 1720 cm^{-1} confirms the presence of carbonyl groups. Furthermore, C-O-C stretching vibrations of different modes are also indicated around 1151 cm^{-1}. And finally, C-H out of plane deformation is observed at 749 cm^{-1}. FTIR spectra of all three PMMA membranes are similar to each other suggesting that the incorporation of ZrO_2 and NiS did not disturbed the structure of PMMA which is used as supporting surface.

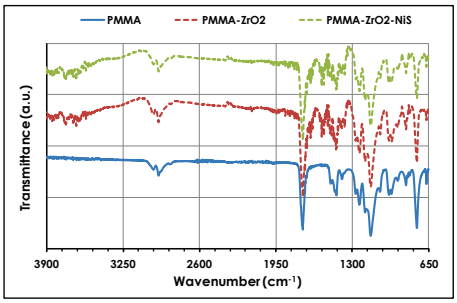

Figure 2: FTIR spectra of PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS membranes.

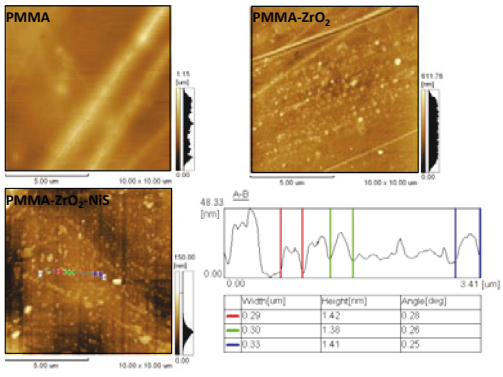

Figure 3: AFM images of PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS membranes, the surface profile of PMMA-ZrO_2-NiS is also shown to calculate average size of NiS nanoparticles.

The surface characteristics of three PMMA membranes were examined by AFM images. Figure 3 shows the height images of PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS. For PMMA, it is clear that the surface is flat and non-porous in nature whereas in case of PMMA-ZrO_2, the suitable dispersion of ZrO_2 powder can be seen in PMMA matrix. Usually, metal oxides are relatively inert therefore, difficult to disperse and often observed as agglomerates in polymer matrix. However, in this case ZrO_2 is uniformly dispersed as shown in figure 3 keeping the optimized ratio between polymer and filler. The AFM image of PMMA-ZrO_2-NiS demonstrates fine distribution of NiS nanoparticles along with ZrO_2. From surface profile of this image, the average size of NiS can be calculated which is around 300 nm. The homogenous distribution of NiS in PMMA matrix shows that the synthesis procedure of PMMA-ZrO_2-NiS is appropriate to uniformly disperse NiS nanoparticles and ZrO_2. This is suitable for achieving high desulfurization efficiency as uniform distribution of NiS is important for enhanced interactions between thiophenes and NiS.

The rebinding performance of as-prepared NiS nanoparticles was tested against DBT as figure 4a shows FTIR spectra of NiS before and after treating with DBT. Since NiS nanoparticles were synthesized via hydrothermal route i.e. by chemical reaction of nickel sulphate and thioacetamide under basic conditions. FTIR spectrum of as-prepared NiS nanoparticles shows a broad band around 3250 cm^{-1} suggesting N-H stretching vibrations of amino groups as breakdown product of thioacetamide associated with NiS nanoparticles furthermore, the band around 1654 cm^{-1} is related to N-H rocking vibrations. A strong peak around 1065 cm^{-1} indicates the formation of sulfur oxygen moieties. From figure 4a, it can be observed that after treating with DBT, NiS nanoparticles exhibited some additional peaks which suggest their rebinding with DBT. For instance, peaks at 2951 cm^{-1} and 2917 cm^{-1} show C-H stretching vibrations additionally, aromatic C=C stretching is also observed from 1652 to 1457 cm^{-1}. The binding between NiS nanoparticles is based on affinity interactions as derived from Pearson concept [13] of soft acid-base combinations. Since NiS is not fully saturated with sulfur therefore, it is expected to interact with sulfur reversibly and FTIR spectroscopic studies indicate the rebinding between NiS and DBT. In order to measure quantitative binding response of NiS for DBT, the absorbance values of standard DBT solutions i.e. in the range of 1-5 ppm before and after treating with NiS nanoparticles is recorded and shown in figure 4b. This graph shows that absorbance of standard DBT solutions decreases at all concentrations after NiS treatment. This suggests that metal sulfide based adsorbent [14] such as NiS nanoparticles in this case can effectively rebind DBT down to 1 ppm which is appreciable for ultra deep desulfurization perspective.

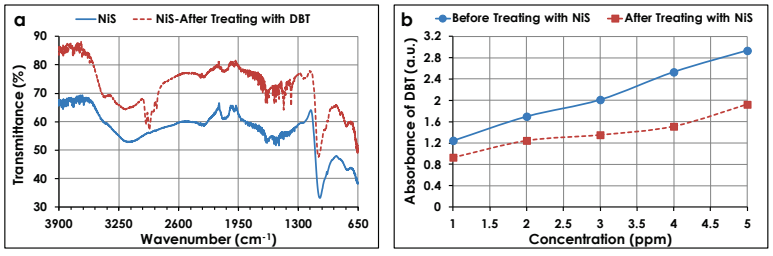

Figure 4: (a) FTIR spectra of NiS nanoparticles before and after treating with DBT (b) absorbance values of standard DBT solutions in the range of 1-5 ppm before and after treating with NiS nanoparticles.

The rebinding tests were further continued by exposing a standard solution of DBT with PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS, separately. The absorbance spectra of standard DBT solution and after treating with different membranes are shown in figure 5. The shift in absorbance is highest for PMMA-ZrO_2-NiS and is least for plain PMMA, while for PMMA-ZrO_2 it is intermediate. This suggests that NiS in PMMA works as affinity material and thus, can effectively rebind DBT while for PMMA-ZrO_2, the decrease in absorbance is intermediate due to some non-specific rebinding by ZrO_2. Finally, plain PMMA does not reflect any appreciable shift in absorbance due to lack of affinity interaction sites.

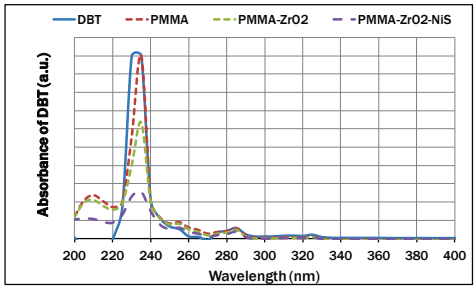

Figure 5: Absorbance spectra of standard DBT solution before and after treating with PMMA, PMMA-ZrO_2 and PMMA-ZrO_2-NiS membranes.

CONCLUSION

NiS nanoparticles appear as suitable recognition material that possesses special affinity for thiophenes due to soft acid-base combinations and these properties make it highly favourable for desulfurization. The process of developing PMMA-ZrO_2-NiS membrane~~s~~ is straightforward which is completed in short time and it does not require special conditions or hazardous chemicals. The developed product offers ease of processing and effective removal of thiophenes at low ppm concentrations under ambient conditions without using hydrogen gas or catalyst. Further optimization in synthetic protocols of present strategy would lead to develop viable and efficient materials for adsorptive desulfurization to produce clean fuels.

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