A Novel Aminated of Divinylbenzene Vinyl Benzyl Chloride Co-Polymers for CO₂ and Water Adsorption-Apreliminary Investigation

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Abstract

Novel amine loaded poly (vinyl benzyl chloride-co divinyl benzene) polymer was synthesized successfully and studied for its CO_2 adsorption and moisture adsorbing efficiency. The poly Vbcl DVB co polymer was loaded with tris (2-aminoethyl) amine in different wt %. Then they were characterized with various physiochemical techniques such as thermo gravimetric analysis (TGA), FT-IR, diffuse reflectance UV spectroscopy (DRS-UV), differeential scanning calorimetric (DSC). Results shown that the polymer synthesized was stable up to 400 °C and can adsorb 4.5 and 6 wt % CO_2 and water at room temperature.

Keywords: aminated, divinylbenzene, polymer, CO₂ adsorption

1. Introduction

The Kyoto protocol identified CO_2 as the most vulnerable greenhouse gas compared to others such as NOx, SOx because its emission and accumulation into the atmospheric is more while comparing to others further it raise cause severe climatic change in earth. But unfortunately for our energy requirement we solely depend coal as source, continuous use of coal as source for energy production ultimately cause rapid accumulation of CO_2 in atmosphere. Recently much work has been devoted for the study on selective removal of CO_2 from the coal-fired power plant flue gas emission. Sorbents work on physical adsorption CO_2 is more impending than the amine or alkali based sorbents because the later needs more energy for regeneration than the former. Silica [1, 2], amine loaded silica [3, 4], metal impreganated silica [5], Zeoliltes [6, 7], metal organic frame work, covalent organic frame work [8-11], covalent triazine based network [12, 13], microporous hyper cross linked polymers [14, 15] were explored in this regards. But yet now none of the above listed sorbents have gained commercial value due to one or more reason such as selectivity, stability, cost or difficulties in the synthesis.

Styrene and its co-polymers and ionic liquid functionalized styrene polymers are more attractive group polymers find applications in various field such as chromatography, insulator and fabricating materials and in gas sorption. Further they find enormous applications as ion exchanger for the removal of toxic inorganic and organic pollutants, and as water purifier [16-20]. Apart from the above, ionic liquid functionalized and amine exchanged VbCl, DVB copolymer resin find application in acid gas adsorbing system. In this regards imidazoline ionic liquid exchanged and amidine tagged resins shows a very good adsorption for CO₂. Imidazoline and amidine functionalization on VbCl resin is little complicated and

economically nonviable process [21-23]. Hence in our present report we planned to synthesis VbCl, DVB copolymer resin and functionalize or cross link the $-CH_2$ -Cl chain of VbCl using tris (2-aminoethyl) amine (tris amine). Amines in general have the property to adsorb water from the atmospheric moisture by their hydrogen bond forming nature in recyclable way. So, in this study we include the study of water as well as CO_2 sorbing capacity of amine functionalized polymeric beads.

2. Experimental

2.1. Materials and Methods

The monomers such as vinyl benzyl chloride and di-vinyl benzene were obtained from Sigma Aldrich Korea and purified by regular literature procedure to remove polymeric inhibitor; polymeric initiator Azobisisobutyronitrile was purchased from Dae-Jung chemicals and recrystallized with methanol before use. Tris (2-aminoethyl) amine (tris amine) was availed from Sigma Aldrich Korea and 1, 4-di-oxane, toluene, PVA were purchased from Dae-jung chemicals and metals Korea.

2.2. Synthesis of Co-polymeric Resin

The VbCl DVB coplolymer resin was synthesized using the regular suspension polymerization technique reported by Ahn et al and Germain et al., here the resin used was utilized the 2.5% divinylbenzene for cross linking, During the suspension polymerization, a mixture consisting of 20.54 g of vinylbenzyl chloride, 0.65 g of divinylbenzene were dissolved in specified quantity of toluene(organic phase) and then 2,2'-azobisisobutyronitrile was added as polymerization initiator about 2% to the monomer weight. The mixture was loaded into a three necked round bottomed flask, one neck was fitted with mechanical stirrer, second one with condenser third neck was connected with temperature sensor. Then about 20 mL of aqueous 2% poly (vinyl alcohol) solution was added as suspending of emulsion forming agent. The polymerization system mixed thoroughly at 300 rpm to get fine spherical distribution of organic phase over aqueous phase finally the mixture was heated to 80 °C for 24 h. The resulting polymer beads were decanted several times in methanol and water, then extracted by Soxhlet extractor using methanol and diethyl ether.

2.3. Amine Exchange

For this, procedure reported by Gandhi et el was adopted. In a typical method about 5 g of above poly VbCl DVB copolymer was made to swell overnight in 70 ml of 1,4-dioxane in 250 ml three-necked flask with a reflux condenser. Tris amine at various wt % (10, 50 and 75%) to the weight of polymer was added into the swollen polymer and the mixture was refluxed for 24 h and left undisturbed for 3 days at room temperature. The resultant product was filtered. After amine exchange, the resin beads were washed thoroughly with copious amount of cold and hot water until the pH of the filtrate was neutral. Then the resin was washed with 1M HCl, water and 1M NaOH for 3 times to remove the Cl⁻ ions on the amines as much as possible.

2.4. Characterization

Here we used a SCINCO thermo gravimeter N-1000 to measure the weight loss of the synthesized polymer before and after amine exchange. A sample weighing ca. 10 mg was loaded into an alumina sample pan in a TG unit and the temperature was programmed to

reach 800 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The TG degradation pure PVbCl DVB copolymer was also taken for comparison. Nicolet 6700 FT-IR spectrometer was used for recording infrared (FT-IR) spectra of the samples room temperature by KBr pelleting technique. Each sample was scanned 20 times over the range 4000–400 cm⁻¹. The nitrogen adsorption–desorption isotherms were measured at 77 K by using a Belsorp mini II (Japan) volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 373 K. The specific surface area, S_{BET}, was determined from the linear part of the BET equation. The pore size and pore volume of the particle were taken from the BET results.

2.5. CO₂ Adsorption

 CO_2 adsorption-desorption measurements using high purity CO_2 (99.999%) and N_2 for the samples using TGA. A sample weight of ca. 10 mg was loaded into an alumina sample pan in a TG unit and the initial activation was carried out at 150 °C for 1 h under a N_2 atmosphere. Then the temperature of sample was brought down to 25, 50 or 75 °C for CO_2 adsorption. The desorption was conducted by gradually raising the temperature from 25, 50 or 75 °C to 150 °C by passing N_2 . CO_2 and N_2 were passed through an automatic valve, assisted with a timer for continuous adsorption or desorption profile respectively.

3. Results and Discussion

3.1. FT-IR

Figure 1 depicts the results of FTIR acquired for the aminated polymer. In both case of polymer (tris 10 wt% and 50% wt %) there where band observed at around 1650 cm⁻¹ attributed to the formation of amino group (-NH). Further the band appeared at 1265 cm⁻¹ indicates that there is an existence of little un-substituted $-CH_2Cl$ groups in the polymer. The formation of a wide broad band between 3347 and 3507 cm⁻¹ is due to the vibrations of N–H bonds in $-NH_2$ groups [24–26, 20].



Figure 1. FT-IR Spectra of Aminated PVbCI-DVB Co-polymers

International Journal of Bio-Science and Bio-Technology Vol.5, No.6 (2013)

3.2. XRD

Figure 2 depicts the wide angle powder XRD patterns of the aminated polymers synthesized. The polymers didn't show any crystalline phase in their morphology. Both of them are exist in amorphous form. We tried to determine the pore structure characteristics using BET technique but unfortunately we didn't get any N_2 adsorption isotherm for both the polymer synthesized which indicates the materials may be nonporous in nature.



Figure 2. XRD Patterns of Aminated PVbCI-DVB Co-polymers

3.3. TGA

To test the stability and to decide desorption temperature during CO_2 adsorption desorption study TGA was carried out. From the results obtained (Figure 3.) it was clearly evidenced that all the polymers synthesized here including DVB-VbCl show good thermal stability up to 350 °C. In case of tris amine loaded polymers there was initial weight loss noted 100 °C temperature this may be due to water occluded in the amino group of the polymers.



Figure 3. TGA of Aminated PVbCI-DVB Co-polymers

3.4. SEM

Figure 4 shows the SEM micrographic images of the amine loaded copolymeric beads, all the polymers resulted with perfect spherical morphology. In high resolution figures shows the interconnected spider web like meshes in side, this web like structures may resulted due to the cross linking of Cl of VbCl by tris amine. Increase in amine content above 50 % wt to the parent polymer was resulted with jelly like structure which is unable to paste over the aluminum stub of SEM hence the micrographs of the same was not given here.



Figure 4. SEM Images of Tris Amine Loaded DVB-VbCI Spheres (a) and (c) Tris-10%, (b) and (d) Tris 50%

3.5. CO₂ and Water Sorption

All the synthesized polymers were subjected to CO_2 adsorption using TG instrument. During the adsorption the polymer loaded with 10% amine and polymer with 70% amine loading were showed a very less adsorption (1-2%) hence the polymer with 50% amine loading was selected for further studies. The low adsorption by the above polymers may be due to low amine content or decreased diffusivity over the 70% amine loaded polymer. Actually the polymer with high amine content will look like a paste hence the amine covered on the surface only adsorb the CO_2 as well as water. In case of 50% amine loading the CO_2 adsorption % was increased up to 6% Figure 5. During the recyclability studies the polymer showed a very good recyclability with stable adsorption and desorption. Water adsorption by the same polymer was up to 4.5 wt%. Water sorption properties of the polymer (usually the poly styrene polymers or non-toxic in nature) may be useful as substitute as an adsorbent to protect the medical equipments and food from the attack of moisture from the environment.



Figure 5. GAS Adsorption Profile of Tris-50% Resin (a) CO₂, (b) Water and (c) N₂

4. Conclusion

Tris amine loaded poly vinyl benzyl chloride divinyl benzene copolymers were synthesized successfully and studied for their ability to adsorb CO_2 and water. From the study it was shown that the polymer with 50 wt% tris amine was more efficient than the other polymers synthesized here. This type of amine loaded polymer was not explored much so far. If explore more they find a wide application in gas sorption industries. Studies on increasing the amine loading without affecting the structure of styrene co-polymer is undergoing in our research.

Acknowledgements

This work was financially supported by grants from Korea CCS R&D centre, funded by the Ministry of Education, Science and Technology of the Korean Government.

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