Synthesis and characterization of amine-impregnated silica gel for potential carbon dioxide (CO$_2$) absorption

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Abstract. The rising of CO$_2$ concentration in atmosphere become global concern due to its effect to the global warming. One potentially economical for CO$_2$ capture is through adsorption using solid sorbents. Silica gel has potential to adsorb carbon dioxide with modification of silica gel with amine groups which provide specific adsorption sides for carbon dioxide adsorption. Therefore, a study of impregnated silica gel with amine for carbon dioxide adsorption was done. A series of characterization was made between raw silica and impregnated silica with amine. Based on the results from Iodine Test Analysis and DSC characterization, it can be stated that the modification of Raw Desiccant Silica Gel (DSG) which had been modified with Aminopropyltrimethoxysilane (APMS), 95% had the highest possibilities of percentage to absorb CO$_2$ from the environment with iodine value of 2736.85 mg/g that indicate the porosity and surface area of the adsorbent is higher. Amine 1A consist of 17.84 % of carbon, 5.41 % of hydrogen and 6.44 % of nitrogen. For FTIR result, Amine 1A has Si-O-Si stretching, C-C stretching, N-C stretching and C-N stretching due to the impregnation of amine to the raw silica gel. From DSC analysis, the higher the peak shows that water molecule bound to Amine 1A evaporated at a higher temperature of 92.4℃ shows the highest porosity and have highest possibility as adsorbent for CO$_2$ adsorption.

1. Introduction

The gradual increase of carbon dioxide concentration has been become a global issue as it is the main cause of global warming and climate changes. This phenomenon started since the industrial revolution in 20th century until carbon dioxide production has been projected to increase from 30 billion tons in 2008 and increasing until 43.2 billion tons in the year of 2035 worldwide [1]. Since then, scientists and engineers have been working out to create more precise and accurate method in measuring carbon dioxide emission to the air. Due to this evolution, chemical adsorption has been used as a major component to absorb carbon dioxide and the innovation of it modification with amine also has become one of the methods to capture carbon dioxide. One of the primary causes of greenhouse emission is the release of carbon dioxide to the atmosphere [2].Carbon dioxide is naturally present in the atmosphere as part of the Earth’s carbon cycle. Nowadays, carbon dioxide is mostly emitted through human activities which also had altered the carbon cycle by adding more carbon dioxide to the atmosphere.

One of the ways to absorb carbon dioxide at the surrounding whether in the air or within the water is by using silica gel. Knowingly, silica gel has been widely used to capture water vapor and keeping things moisture-free. For domestic usage, typically, users will hang a bag of silica gel in a wardrobe or shoe...
rack. This is in order to prevent the respective area from emitting any musty smell. However, for industrial usage, silica gel has been used in various ways such as in water absorption chiller [3] and dehumidification of air conditioning system [4]. This is because due to their good adsorbents capabilities which are affected by the large surface area and the porosity properties which had an equal pores distribution. Silica gel also was proved to have superior qualities in chemical and physical properties [5]. Silica gel also had been used in the process of removal of hardness in wastewater treatment [6], [7] and the adsorption of p-nitrophenol in water pollution which is a typically an encountered pollutant. Desiccant silica gel also known as the medium of the adsorption of octamethylcyclotetrasiloxane for biogas purification [8].

Studies by [9-11] had found that the impregnation of silica gel with amine is the most favorable method to capture the carbon dioxide content. This is due to their reasonable cost, high capacity of adsorption of carbon dioxide and they had a low adsorption heat and specific heat capacity needed [5]. By using this solid modified adsorbent, it also can remove contaminant especially hardness in the water such as mercury [6]. Quang et.al [9], had conducted a study for carbon dioxide capture based on the impregnation of amines. In this study, they used 2-aminomethylpropanol (AMP), monoethanolamine (MEA), diethanolamine (DEA) and polyethylenimine (PEI). The purposes of this study are to investigate the thermal stabilities, adsorption capacity, heat capacity and adsorption of heat. The results had shown that the impregnation of MEA-silica adsorbent had the highest capacity of adsorption of carbon dioxide compared to the other amines.

Therefore, the objective of this research is to synthesize and characterize the carbon dioxide absorption capabilities by method of impregnation of the amine with the desiccant silica gel (DSG) which will be compared to the raw DSG. Correspondingly in this research, DSG will be impregnated with different amine such as 3-aminopropyltrimethoxysilane (APMS), 95%, Diethylenetriamine (DEA) and 3-(triethoxysilyl)-propylamine (TEPA) in order to produce amine-impregnated solid adsorbents.

2. Methodology

2.1 Impregnation of amine-silica gel

Amine impregnated silica gel were prepared by using raw silica gel. A desired amount of APMS with 50 wt% which will be labelled as Amine 1A, was dissolved in distilled water to prepare the impregnation solution. Accordingly, 4g of the impregnated amine solution is poured into a beaker containing 1g of desiccant silica gel and stirred for 10 minutes. The mixture is then heated on a hotplate at 90˚C and will be increase the temperature by 5˚C for each 5 minutes till it reached 115˚C. Then, the mixture will be left drying in an oven for 2 hours at 105˚C to remove any possible moisture left [12]. Table 1 listed the composition of various amine with different percentage and types of amine.

| Sample   | Types of amine use          |
|----------|-----------------------------|
| Amine 1A | 50% of APMS                |
| Amine 1B | 60% of APMS                |
| Amine 2A | 50% of diethylenetriamine  |
| Amine 2B | 60% of diethylenetriamine  |
| Amine 3A | 50% of 3-(triethoxysilyl)-propylamine |
| Amine 3B | 60% of 3-(triethoxysilyl)-propylamine |

2.2 Characterization of samples

2.2.1 Differential Scanning Calorimetry (DSC)

Modeled DSC 6000 Perkin Elmer is used to measure the melting point and the enthalpy changes of the sample. It is measured starting from 30 ˚C to 200˚C. The nitrogen gas was used with the flow rate of 20mL/min at 10˚C/min. The endothermic peaks of the modified silica will be shown by the DSC curves. The result of the enthalpy value ranges will also be shown by the DSC.
2.2.2 Elemental Analysis
The purpose of this method is to analyse the presence of carbon, nitrogen, hydrogen and sulphur in raw DSG and the impregnated amine-silica gel. The elemental analyzer used for this method is Perkin Elmer 2100 series II CNH/S analyser [16].

2.2.3 Fourier Transform Infrared (FTIR)
Fourier Transform Infrared (Bruker Vertex 70) Spectroscopy is used to evaluate the presence of amine and other contaminant present for the DSG and the modified one. For FT-IR results, raw DSG and modified DSG were prepared by measuring in transmission mode. The sample is examined by a transmission electron microscope which operates at 200 KV [10]. FTIR spectra [4000-600 cm⁻¹] were collected with resolution of 1 cm⁻¹ by CO-adding 64 scans for each spectrum.

2.2.4 Iodine Test Analysis
Iodine Tet Analysis is About 12.5g of anhydrous sodium thiosulphate was weighed and dissolved in a 500mL of volumetric flask with distilled water. 0.1g of raw DSG was weighed and taken to 250mL of conical flask. Then, the flask was put in a incubator shaker for about 2 hours at 105˚C to ensure the equilibrium absorption of iodine. After that, the flask was taken out to undergo filtration process. After being filtrate, the filtrate will be titrated with the 0.1N sodium thiosulphate until the yellowish brown of the iodine solution from the flask will turn colourless. The data will be recorded and the iodine value will be calculated in the equation below.

\[
\text{Iodine Value} = \frac{(\text{mL} \ 0.1N \ Na_2S_2O_3 \ \text{Blank} - \text{mL} \ 0.1N \ Na_2S_2O_3 \ \text{Test}) (12.7)}{0.1}
\]

Where, the mL 0.1N Na₂S₂O₃ Blank = the volume of sodium thiosulphate required to titrate the blank solution.

the mL 0.1N Na₂S₂O₃ Test = the volume of sodium thiosulphate required to titrate the test solution that contained the sample.

12.7 = the amount of grams of iodine contained in 1L of 0.1N iodine solution

0.1 = the amount of the sample in grams

3. Result and Discussion
3.1 Differential Scanning Calorimetry (DSC)
For DSC analysis, the samples melting point curve, which were used to determine the enthalpy changes of the phase transitions can be observed from the graph of each samples. Figure 1 show the DSC curves for raw DSG and amine modified silica gel. From the figure it can be seen that the raw DSG has the lower peak which shows that the raw DSG has lower porosity compare to the amine impregnated silica gel. When the raw DSG has modified with the addition of amine, it can be observed that the peak has been increased. From the figure, Amine 1A has the highest peak which mean that it has higher porosity compare to others. The peak temperature for each samples were summarized in Table 2 that shows the endothermic peaks, represent the removal of physically bound water [17]. These were further confirmed by the enthalpy values as shown in Table 2.
Figure 1. DSC curves for raw DSG and amine modified silica gel
From Table 1 below, it can be seen that Amine 1A has the highest value in term of peak temperature, peak energy height, peak area and $\Delta H$. The higher the peak area shows that water molecule bound to Amine 1A evaporated at a higher temperature of 92.4°C. Therefore, sample Amine 1A had the highest specific surface area compared to others sample that simply explain by its higher water adsorption capacity [17]. Sanchez-Zambrano et. al., [13] had stated that, the energy consumption of the sample affects the adsorption of CO$_2$. This is because of the physical water bound for the sample is hard to suppress. Hence, the need of energy is required in order to break the bond which will be resulted to transition of the sample. From the Table 1 also, it can be seen that the peak temperature for Figure 1.1 indicates the melting point of each of the respective samples since silica gel is not an organic compound [14].

| Sample         | Raw DSG | Amine 1A | Amine 1B | Amine 2A | Amine 2B | Amine 3A | Amine 3B |
|----------------|---------|----------|----------|----------|----------|----------|----------|
| Peak temperature (°C) | 72.85   | 92.4     | 82.77    | 79.43    | 92.1     | 86.99    | 74.62    |
| Peak Energy Height (mW) | 1.392   | 4.751    | 4.026    | 3.516    | 4.432    | 1.936    | 2.661    |
| Peak Area (mJ) | 394.855 | 1757.5   | 1447.142 | 953.981  | 1246.527 | 509.991  | 729.06   |
| Enthalpy, $\Delta H$ (J/g) | 65.809  | 292.917  | 241.19   | 158.997  | 207.754  | 84.998   | 121.52 |

3.2 Elemental Analyser (EA)

Elemental analysis based on Table 3 shows below, that almost none presence of carbon and nitrogen for the raw silica gel. The modification of the raw silica gel using different amine solution makes it possible for this characterization to take place and thus to observe the difference between raw and modified silica gel. After the modification takes place the content of carbon, hydrogen and nitrogen shows an increase as the amines are grafted on the surface of the silica gel. The increment of nitrogen is due to the amine structure that contain a basic nitrogen atom with a lone pair [15]. Meanwhile, for the increment carbon is due to the derivation of ammonia with a substituent such as alkyl group by replacing one or more hydrogen atoms.

| Sample         | Carbon | Hydrogen | Nitrogen |
|----------------|--------|----------|----------|
| DSG            | 0.21   | 1.98     | 0.23     |
| Amine 1A       | 17.84  | 5.41     | 6.44     |
| Amine 1B       | 18.26  | 5.89     | 6.91     |
| Amine 2A       | 15.72  | 4.61     | 9.69     |
| Amine 2B       | 15.66  | 5.11     | 9.67     |
| Amine 3A       | 16.19  | 4.98     | 5.91     |
| Amine 3B       | 17.22  | 5.29     | 6.36     |
3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2 below shows the Fourier-Transform Infrared Spectroscopy results for raw desiccant silica gel (DSG) and modified silica gel with amine by using Perkin Elmer FT-IR. As shown by Figure 2 below, raw dessicant silica gel has the lowest number of band peak occurrence which means that the raw DSG has not yet been modified with amine. For the raw silica gel, it shows the fewest band peak in the graph. A slight peak is seen near band 1600-1650 cm\(^{-1}\). Next, the highest band peak for all of the graph is at band 1000-1200 cm\(^{-1}\) [16]. This band is assigned to Si-O-Si stretching and also means that the biggest the sample is mainly made of silica.

Meanwhile, for all the modified silica gel with amine, show that there are significant changes to the peak occurrence on the samples. As seen from the graph for Amine 1A, Amine 1B, Amine 3A and Amine 3B, it shows that there are band peaks of wavenumber around 1500 cm\(^{-1}\) (the red oval). These bands are assigned to N-C stretching modes, respectively [18]. Also this is because of the presence of tertiary amine in the silica. Amine 1 is 3-Aminopropyltrimethoxysilane (APMS) 95% and amine 3 is 3-(triethoxysilyl)-propylamine (TEPA). This concludes that the loading of Amine 1 and Amine 3 is successful. Next, as seen in Amine 1A, a few peak of band is seen. One of it shows in the band range of 2800-3000 cm\(^{-1}\) (the blue oval), and since these bands are also assigned to N-C stretching mode it means that the presence of amine salt is detected. The same result is seen at Amine 3.

For Amine 2A and Amine 2B, it has been seen that there is a slight increase near band 2800-3000 cm\(^{-1}\) (the blue oval). Then, there is a high peak near band 1600 cm\(^{-1}\) (the black oval). There is a C-C stretching and it indicated that presence of alkene is detected. This is maybe due to the presence of alkene in DEA that makes the band peak high. This can be seen on both for Amine 2A and Amine 2B. Lastly, there is a slight peak at band 1266-1342 cm\(^{-1}\) (the green oval) for all modified silica amine. These bands are assigned to C-N stretching and indicate that the presence of aromatic amine is detected. Also the presence of amine could also be detected near band 1580-1650 cm\(^{-1}\). This band is assigned to N-H bending. This also is seen on all modified silica gel graphs.

3.4 Iodine Test

Table 4 below shows the iodine number of the samples for DSG and modified DSG with amine. Iodine number estimate of its surface area and porosity [19]. The minimum iodine number for adsorbent is 950 mg/g [20]. The higher the iodine number, the better adsorption of the adsorbent. Iodine number is mass of iodine in g that is consumed by 100 g of a chemical substances. From Table 4, raw silica shows the least iodine value which prove impregnated silica with amine will increase the porosity, therefore will increase the adsorption of carbon dioxide gas. The highest iodine number is Amine 1A with 2736.85 mg/g. When the DSG were modified with amine the potential absorption of carbon dioxide will
increase. Most of modified amine have iodine number more than 2400 mg/g which how the impregnation of amine has been increase the surface area and porosity of the adsorbent.

Table 4. Results for Iodine Test for Raw DSG and amine modified silica gel

| Type of solution | Sodium thiosulphate blank (mL) | Sodium thiosulphate test (mL) | Iodine value (mg/g) |
|------------------|--------------------------------|--------------------------------|---------------------|
| Raw DSG          | 25                             | 9.90                           | 1917.70             |
| Amine 1A         | 25                             | 3.45                           | 2736.85             |
| Amine 1B         | 25                             | 4.00                           | 2667.00             |
| Amine 2A         | 25                             | 5.70                           | 2451.10             |
| Amine 2B         | 25                             | 5.10                           | 2527.30             |
| Amine 3A         | 25                             | 3.80                           | 2730.50             |
| Amine 3B         | 25                             | 4.60                           | 2590.80             |

4. Conclusion
The research had shown that by characterizing the impregnation of raw DSG with amine managed to improve the carbon dioxide absorption capabilities. From the discussed results stated from Iodine test characterization, which being supported by the DSC results, it can be seen that the results of characterizing the impregnation of raw DSG with Amine 1A, which is Aminopropyltrimethoxysilane (APMS) 95%, with the wt% of 50 has the highest potential of CO$_2$ absorption compared to the other tested samples which are the amine 2, which is Diethylenetriamine (DEA) and amine 3, which is 3-(triethoxysilyl)-propylamine (TEPA). Correspondingly stated, further research is in need in order to get the finalize results of which of the methods which was being used by the other authors are the best solution to manage the CO$_2$ absorption which could benefits the future in term of environmental safety or the economics system.

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