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CARBON DIOXIDE SORPTION BY TETRADECYLAMINESUPPORTED ON SILICA GEL

(Serapan Karbon Dioksida Oleh Tetradesilamina Disokong Pada Silika Gel)

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Abstract

Carbon dioxide emissions generated from fossil fuel-based power plants and other industries has reached 400 ppm in atmosphere. This negatively impact the environment, infrastructures and wildlife in particular. A lot of efforts are needed to produce CO_2 gas sorbent in order to reduce high CO_2 concentration. Therefore, porous silica gel (SG) is modified with amine compound for carbon dioxide capture. Calcinated silica gel functionalized with tetradecylamine (TDA) using wet impregnation has been developed as a porous media. The prepared sorbents is characterized by N_2 physisorption technique Brunauer-Emmet-Teller analysis (BET). Significant changes in physical properties of the sorbents further ascertained the dispersion of TDA on the internal channels and external surface of the SG. Reactivity of porous sorbent towards CO_2 was evaluated using isothermal CO_2 adsorption desorption technique. This study shows 65TDA/SG enable to adsorb CO_2 in the highest capacity which is 23.22 cm^3 CO_2 per gram sorbent. Moreover, CO_2 capture consists of two type sorption which are physisorption and chemisorption. 55TDA/SG is the best sorbent in capturing CO_2 by chemisorption (19.62 cm^3 CO_2 per gram adsorbent).

Keywords: tetradecylamine, modified silica gel, carbon dioxide, chemisorption, physisorption

Abstrak

Pembebasan karbon dioksida terhasil daripada plan penghasilan tenaga berasaskan bahan api fosil dan pelbagai industri telah mencecah kepekatan 400 ppm di atmosfera. Perkara ini memberi kesan negatif kepada alam sekitar, infrastruktur dan kehidupan liar khasnya. Pelbagai usaha diperlukan untuk menghasilkan penjerap gas CO_2 dalam usaha untuk merendahkan kepekatan CO_2 yang semakin meningkat ini. Oleh itu, silika gel berliang (SG) telah di ubahsuai dengan sebatian amina untuk pemerangkapan karbon dioksida. Silika gel yang telah dikalsin akan difungsikan dengan teteradesilamina (TDA) menggunakan kaedah impregnasi basah telah dibangunkan sebagai media berliang. Penjerap yang dihasilkan akan dicirikan dengan teknik jerapan fizikal N_2 iaitu analisis Brunauer-Emmet-Teller (BET). Perubahan ciri fizikal yang ketara pada penjerap mengukuhkan lagi sebaran TDA pada permukaan dalam liang dan juga permukaan luaran SG. Kereaktifan penjerap berliang terhadap CO_2 telah dinilai menggunakan teknik penjerapan dan penyahjerapan isoterma CO_2. Hasil kajian ini menunjukkan bahawa 65TDA/SG mampu menjerap CO_2 dalam kapasiti yang tertinggi sebanyak 23.22 cm^3 CO_2 per gram penjerap. Tambahan, pemerangkapan CO_2 terdiri daripada dua jenis serapan iaitu serapan fizikal dan jerapan kimia. Penjerap 55TDA/SG adalah penjerap terbaik dalam pemerangkapan CO_2 secara jerapan kimia (19.62 cm^3 CO_2 per gram penjerap).

Kata kunci: tetradesilamina, SG di ubahsuai, karbon dioksida, jerapan kimia, serapan fizikal

Introduction

In the era of globalization, carbon dioxide (CO_2) is well known as a main greenhouse gas. This gas is released into the atmosphere from human activities, industrial development including fossil fuel burning, chemical and petrochemical manufacturing as reported by [1]. Indoor air pollutants (IAPs) included that CO_2 is the representative pollutant of indoor air quality and its concentration is associated with the human activities while the outdoor concentrations of CO_2 range from 350 – 450 ppm. Therefore, studies have been done to collect CO_2 gas to be used as fuel feedstock and other chemicals. The great effort in reducing concentration of CO_2 in atmosphere is more important rather than lowering concentration of CO_2 gas emission [2]. The accumulated CO_2 traps the earth's heat, thus creating global warming which has already altered weather patterns and further increasing sea levels due to the melting of the polar iceberg. There were several works reported in reducing CO_2 concentration by capture and separate the CO_2 gas. There are different unit operations such as liquid absorption phenomena [3], solid adsorption [4-6], cryogenic techniques and selective diffusion through polymer, metallic or ceramic membranes [7].

Therefore, research in developing CO_2 sorbents must be taken in order to reduce the concentration of CO_2 in the atmosphere. Amines are the most widely used organic chemicals for CO_2 capture due to their basicity. This allows them to react with acidic CO_2 to form a carbamate compounds. This reaction known as chemisorption. Previous study, straight chain alkylamine with C18 known as octadecylamine was developed as CO_2 sorbent. Octadecylammonium octadecylcarbamate ion pairs (alkylammonium alkylcarbamate) was formed on contact with dry CO_2 [8]. Belmabkhout et al. [9] reported, under dry conditions, carbamate with CO_2/N stoichiometry ratio of 0.5 is formed. This means two amine groups are needed in interact with one CO_2 molecule on the adsorbent surfaces as reported by Gray et al. [10] (refer Equation 1).

$$\underset{\text{alkylamine}}{2\,RNH_2} + \underset{\text{carbon dioxide}}{CO_2} \longrightarrow \underset{\text{alkylacarbamate}}{RNHCO_2^-} + \underset{\text{alkylammonium}}{RNH_3^+} \quad (1)$$

Nowadays, porous materials are widely used as supporter such as silica dioxide, silica gel, activated carbon and many more [1, 2, 4, 6]. Supporter is important to improve stability of the amine compound. Besides, porous materials have an ability to interact with CO_2 gas through physical interaction (physisorption). In this study, physical and chemical modifications at the external surface or internal channels of the supporter (silica gel, SG) using organic functional groups (tetradecylamine, TDA, $C_{14}H_{31}N$) have drawn much attention. The synthesized sorbents were characterized by Brunauer-Emmet-Teller analysis (BET).

Materials and Methods

Modification of silica gel (SG) by tetradecylamine (TDA) represented as TDA/SG was done through wet impregnation method with few modifications [11]. Silica gel powder (Fluka) was calcined at 600 °C for 3 hours before impregnation process with various percentage of TDA (ALDRICH®, 97%) and chloroform, $CHCl_3$ (SYSTERM®, 99 – 99.4%) as a solvent. After stirring for 4 hours in a closed system, the mixture was rested for 1 hour before sonication (S 4000-010 Sonicator 4000) and afterward evaporated in air for one night. The process followed by drying at 45 °C for 4 hours in a vacuum oven. Lastly, the adsorbents were physically characterized by N_2 adsorption desorption isothermal and reactivity towards CO_2 measured by CO_2 adsorption desorption isothermal at 30 °C using BET technique (Micrometiric ASAP 2020).

Results and Discussion

The sorption capacity of CO_2 on prepared sorbents were measured by CO_2 isothermal adsorption desorption using BET technique at 30 °C. Referring to Figure 1 and 2, unmodified SG was able to captured 9.39 cm^3 CO_2 / g sorbent. This capacity is higher than another two modified SG, 5 and 15TDA/SG. Addition of 5-15 % TDA will prevent direct interaction of CO_2 towards SG due to formation of mono or multilayers TDA on SG surfaces. This happened during wet impregnation process in which mixture of TDA and chloroform were able to wet entire surface of SG including external and internal surfaces (small pores of SG). After drying process, chloroform was evaporated and TDA layers formed on the SG surfaces. It was clearly shown that pure SG is enable to adsorb CO_2. According to addition of 15 to 65 % TDA, the amount of CO_2 uptake increased proportional to the TDA percent loaded. The capacity of CO_2 gradually increased from 13.21 up to 23.22 cm^3 CO_2 / g sorbent. However, CO_2 uptake by the SG modified with 75 % TDA was reduced drastically and lower than 45TDA/SG sorbent.

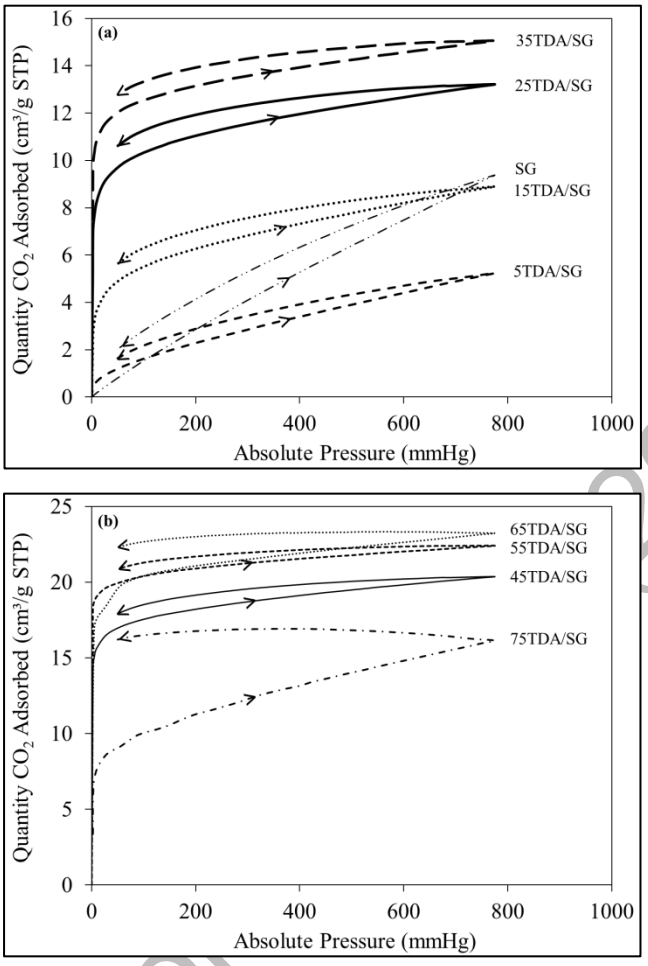


Figure 1. CO_2 adsorption-desorption isotherms of SG and modified SG with (a) SG, 5TDA/SG, 15TDA/SG, 25TDA/SG and 35TDA/SG and (b) 45TDA/SG, 55TDA/SG, 65TDA/SG and 75TDA/SG

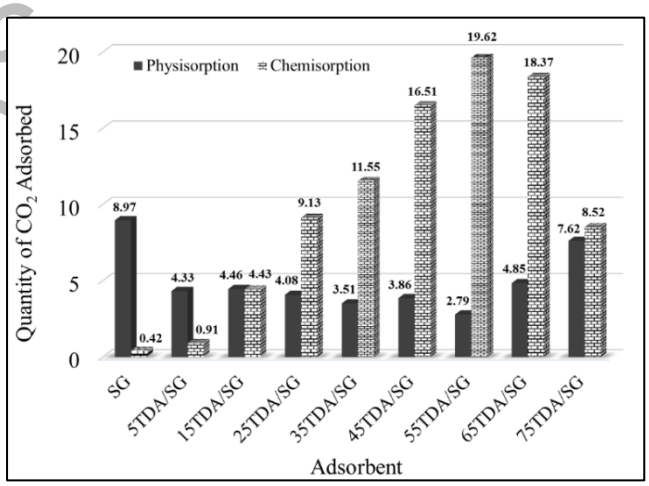


Figure 2. Quantity of CO_2 adsorbed physically and chemically measured by CO_2 adsorption desorption isothermal using BET technique

At a very low pressure, CO_2 sorption curve is very sharp and increased drastically around 0 – 20 mmHg. Formation of linear curve can be seen at higher pressure (more than 20 mmHg). This pattern is just applicable for modified SG whereas CO_2 sorption curve for unmodified SG sorbent was increased gradually without linear curve at the higher pressure. Shaw et al. [12] reported a very sharp sorption curve at the initial pressure showed that sorption of N_2 gas occurred in the small pores which known as micropores. Referring to Table 1, measured surface value t-plot$_{mic}$ for SG is 12.89 m^2/g and this proved SG contained small pores in micro size known as micropores. In this research which involved CO_2 gas, the very sharp curve proved that the CO_2 gas were able to enter the micropores of SG. It happened due to strong interaction between internal SG channels (micropores surfaces) towards CO_2 gas. This interaction known as physical interaction or so called physisorption. However, drastically increased CO_2 uptake at the initial sorption also clarified chemical reaction that formed between CO_2 and TDA molecules. This chemical reaction also known as chemisorption and can produce another compounds such as alkylcarbamate and alkylammonium. Bacsik et al. [13] suggested highest amount of CO_2 uptake happened at highest pressure and lower temperature by modified silica with (3-aminopropyl) methyldiethoxysilane (APMDES) was referred to chemical adsorption of CO_2.

There are two lines on the sorption curve which refers to adsorption (->-) and desorption (-<-) line. Adsorption line starts from 0-760 mmHg whereas desorption line is vice versa (760 – 0 mmHg). Referring to the curve, we found desorption line is not converge with the adsorption line at lower pressure. This explained by changing pressure of the system was unable to fully desorp the captured CO_2 gas. Usually, this refers to CO_2 gas that entered micropores and chemically bonded with the TDA molecules. Therefore, energy (usually heat energy) is needed to break these chemical bonds. Therefore, captured CO_2 gas can be desorbed and sorbent can be used again in capturing CO_2.

Table 1. Effect of percent TDA loading towards SG surface properties

Adsorbent	**S_{BET} (m^2/g)**	**t-plot$_{mic}$ (m^2/g)**	**V_t (cm^3/g)**	**W_D (Å)**
SG	246.17	12.89	1.2	174.9
5 TDA/SG	194.7	n.d	0.9	121.8
15TDA/SG	159.6	n.d	0.7	111.2
25TDA/SG	128.8	n.d	0.5	91.5
35TDA/SG	113.2	n.d	0.4	87.9
45TDA/SG	81.4	n.d	0.2	81.0
55TDA/SG	61.3	n.d	0.2	73.0
65TDA/SG	48.8	n.d	0.1	71.0
75TDA/SG	29.2	n.d	0.1	67.5

n.d = note detected

Figure 2 shows quantity of CO_2 adsorbed that measured by adsorption desorption of CO_2 using BET technique. As discussed earlier, CO_2 sorption at initial pressure (0 – 20 mmHg) was corresponded to chemisorption and physisorption in the micropores. Therefore, by subtracting capacity of CO_2 at the highest pressure (760 mmHg) to the value at lower pressure, the amount of CO_2 captured by physical interaction can be measured. CO_2 uptake by physisorption on SG was the highest compared to other sorbents with value 8.97 cm^3 CO_2/g sorbent. This value explained that SG is a porous material which able to attract and capture CO_2 gas in the SG pores through physical interaction. The absence of sharp sorption curve at the initial pressure proven physisorption was primarily occurred compared to chemisorption (0.42 cm^3 CO_2/g sorbent).

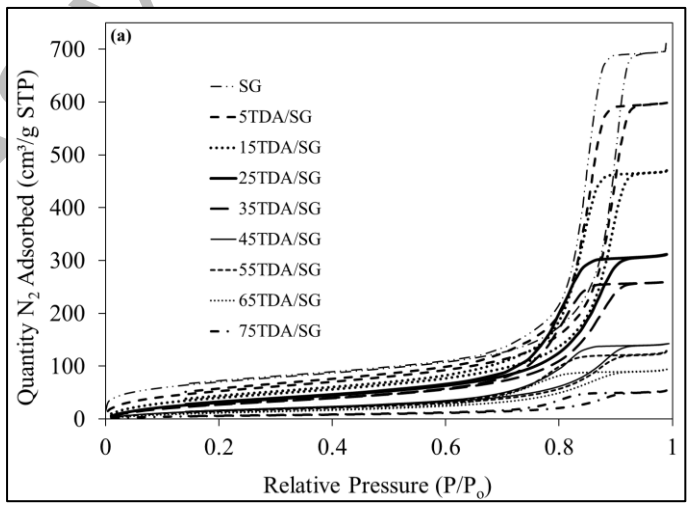
Addition of TDA from 5 to 55 % exhibited an increasing capacity of chemisorption from 0.91 to 19.62 cm^3 CO_2/g sorbent. Meanwhile, capacity of physisorption was reduced gradually with increasing percent of TDA. This clarified as amine was loaded onto SG, the pores of SG are filled with amine layers hence increasing the steric hindrance for

physisorption of CO_2 to occur and more CO_2 affinity sites were exposed for chemisorption to take place [14]. Thus, it is suggested that the higher sorption of CO_2 on modified SG also due to more chemisorption process occurred in the internal channels and external surfaces (CO_2–TDA chemical interaction/reaction).

However, capacity of CO_2 sorption by SG loaded with 5 and 15% TDA are not improve significantly compared to ability of pure SG since the presence of TDA layers on the internal SG pores have reduced the CO_2–SG physisorption and yet improved chemisorption. Conversely, CO_2 uptake by chemisorption on higher percent TDA loading (65 and 75TDA/SG) was declined to 8.52 cm^3 CO_2/g sorbent whereas capacity of physisorption was take place by increased up to 7.62 cm^3 CO_2/g sorbent. Hence, addition of high amount of amine (more than 55% TDA) is not require due to formation of amine double or multilayer on the SG surfaces which reducing amount of active sites and further dropping the ability of formation alkylammonium alkylcarbamate compounds [15].

Amine modified SG was further examined using physisorption analysis (Micrometiric ASAP 2020). BET surface area, micropore surface area (t-$plot_{mic}$), pore volume and pore width values was summarized in Table 1. Figure 3(a) shows N_2 adsorption and desorption isotherms of all adsorbents. According to IUPAC (1972), the hysteresis curve of all adsorbents is type A where the mesopores are cylindrical in shape [16]. At the earlier stage of the sorption, which is involving low pressure, the adsorption of a single/mono layer of N_2 happened inside pores and followed by adsorption of multiple layers at higher relative pressures. Based on the isotherms, as the TDA loading percentage increases, the quantity of N_2 sorbed will decreases. This is due to physical changes that occurred on the SG surface after the impregnation of TDA. According to rapid pore filling theory, the long chain molecules (TDA) can rapidly fill into the mesopores. Consequently, it creates pore blockage and resulted in the lowering of the quantity of N_2 adsorbed which is directly refers to the decreasing in BET surface area.

Referring to Figure 3(b), average pore diameter appeared as a peak for each sorbent. The highest peak was the SG without any loading while the lowest peak was the 75TDA/SG. The average pore width of SG is 174.9 Å, which refers to the aperture or diameter of the mesopores. When the SG was modified with 35% TDA, the average pore width shifted to a lower value (100.42 Å) since the formation of TDA layer on the inner wall of the mesopores. This result suggests that more molecules are able to get into the pores during modification even though TDA is a straight and long chain molecules. Moreover, the addition of 75% TDA shows drastically decreased in pore volume which is from 1.2 to 0.1 cm^3/g (Figure 3(c)). This explains the rapid entrance of amine molecules into the pores making the empty spaces to be filled with that amine molecules [17, 18]. Therefore, the decreasing values of average pore width are proportional with the total volume of the pores.



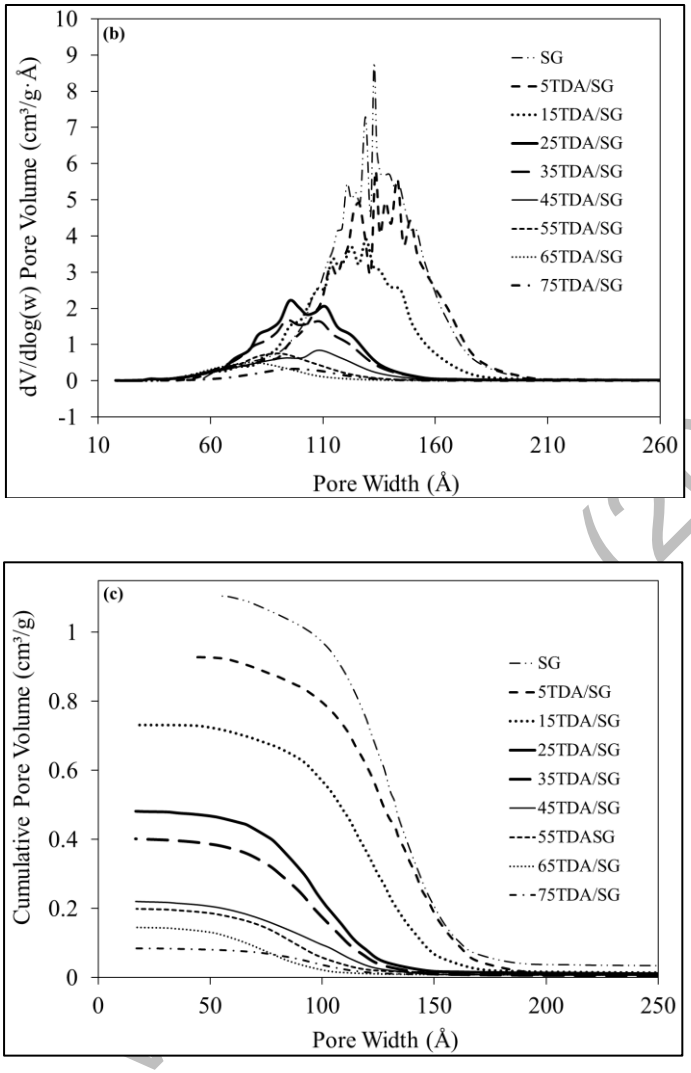


Figure 3. Surface properties of SG and modified SG (5TDA/SG, 15TDA/SG, 25TDA/SG, 35TDA/SG, 45TDA/SG, 55TDA/SG, 65TDA/SG and 75TDA/SG by BET technique with (a) N_2 adsorption desorption isotherms, (b) Pore size distributions and (c) Cumulative pore volume of sorbents.

Conclusion

CO_2 gas can be captured by prepared sorbent which is SG modified with different percentage of TDA. CO_2 isothermal adsorption desorption analysis shows that capturing CO_2 gas involved two types of sorption (physisorption and chemisorption). SG is a porous material acts as supporter and able to physically capture CO_2 gas whereas modified SG are mainly undergo chemically capture CO_2 gas. Moreover, 55TDA/SG was the optimum sorbent due to its ability in capturing highest amount of CO_2 through chemisorption. It is very important in order to increase retention time of CO_2 on the sorbent before it finally being desorb at different time and place (good for transport purposes). Various amount of TDA loading resulted in great changes in physical properties of the adsorbents in term of BET surface area, average pore diameter and total pore volume of adsorbents. Therefore, all significant changes happened actually ascertained the existence of TDA on the SG surfaces by wet impregnation method.

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