Sorption equilibria of CO_2 on synthesized CaO in the presence of water

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Abstract

Calcium-based adsorbents produced by biomass material is technically feasible, costly effective and advantageous to a certain extent in capturing CO_2. Since the waste of a cockle shell is found to contain around 98% calcium, it can be a good source for $CaCO_3$ and yield CaO through the high temperature calcination process. The sorption equilibria of CO_2 on synthesized CaO with different amounts of water were measured experimentally by using a volumetric method at a temperature of 2°C. Under dry conditions, synthesized CaO has a low CO_2 uptake, as the adsorption rate of CO_2 in calcium-based sorbent is high at higher temperatures. While under wet conditions, the large increment of CO_2 adsorption was observed due to formation of CO_2 hydrates which were indicated by inflection of isotherms at a definite pressure of the S-shape. At the inflection point, the highest sorption capacity (5.07 mmol/g) was obtained at a water ratio of 0.55, which is about 30 times higher than dry samples. The trend of FTIR spectra were observed to be similar for raw cockle shells and wet CaO after CO_2 adsorption, in contrast with spectra of CaO before adsorption. The formation of CO_2 hydrate can be further verified by the changes of surface morphology of CaO, before and after adsorption. It can be concluded that calcium-based sorbent with the presence of water has the ability to be further utilized for CO_2 separation.
Keywords: CO_2 emission, sorption equilibria, gas hydrate, cockle shell, calcium oxide.

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1 Introduction

1.1 Carbon dioxide emission

Excessive emissions of carbon dioxide in the atmosphere as prevalent greenhouse gas may induce global warming and has become a major challenge for this century to control the CO_2 emission. High research effort is needed in order to find ways to reduce the large amount of CO_2 emitted to the atmosphere. Thus, carbon capture and sequestration (CCS) is becoming highly important process to ensure the world sustainability. The CCS is a process of capturing waste CO_2 from large point sources and storing the captured CO_2 safely [1]. Several options for CO_2 removal have been suggested to reduce the large amount of CO_2 emitted to the atmosphere. One of the proposed solutions is by sequestering CO_2 in the deep ocean by formation of gas hydrates in porous media [2, 3]. It could be a potential method to store CO_2 as CO_2 hydrates can be formed in the sea deeper than 400 m [1]. However, the large concentration difference of CO_2 in hydrates and in the surrounding natural seawater renders the naked CO_2 hydrates unstable. This potential dissolution of CO_2 hydrates could be reduced or at least made to take place over a longer time frame if the carbon dioxide were injected into porous media where the fluid flow was restricted. Large amounts of experimental data are available focusing hydrate formation under bulk conditions, only a few studies have addressed hydrate formation in porous media. Activated carbon and silica gel are two porous media often used in the recent studies [1, 3–5]. Wang *et al.* [1] measured the sorption behaviour of CO_2 and CH_4 on activated carbon with a wide pore-size distribution at 275 K in different amount of water content. They observed that there were an inflection pressures at about 1.5–2.0 MPa and at 3 MPa on sorption isotherms of CO_2 and CH_4; respectively to indicate hydrate formation in the system. Zheng and his co-workers have reported that the formation of CO_2 hydrates were influenced by the quantity of pre-sorbed water and pore size distribution of the silica gel [3]. Only the pores with a definite size are suitable for hydrate formation as the impetus of pore space for hydrate formation disappears if the pore size is too large [1, 3]. A less amount of water was used for hydrate formation in silica gel as compared with activated carbon due to the strong H-bonding between the water and the silicon hydroxyl group on the surface [3].

1.2 Calcium-based sorbent

The cost of porous materials is become a crucial factor to be considered for the potential application of CO_2 sequestration. The success of this approach is dependent on the development of low cost sorbent with high selectivity and adsorption capacity. In the present work, the calcium-based sorbent which is rooted from biomass material has been suggested as a potential CO_2 adsorbent as it is technically feasible, cost effective and advantageous to certain extent in capturing CO_2 [6, 7]. Seashell is found to be reliable potential biomass source for calcium carbonate ($CaCO_3$) since process of mining large quantities of raw materials such as limestone result in extensive deforestation and top soil loss [8]. Li *et al.* [9] have reported that CaO composition in seashell is higher than limestone. As waste cockle shell (CS) is abundantly available in Malaysia, the utilization of this calcium-based as CO_2 adsorbent should be expanded in this work. Calcium oxide can be extracted from cockle shell via thermal decomposition process as it contains a large amount of $CaCO_3$. The process is also known as calcination, where it uses heat to decompose the material and cause volatile removal or phase transition (endothermic reaction) for producing synthesized CaO and CO_2 [10]. Calcination can be carried out in lime kiln, tube furnace and thermal gravimetric analyzer (TGA). As the significance amount of water is added to the synthesized CaO, a very exothermic reaction is occurred and calcium hydroxide is formed as shown in Eqn. (1) [11]:

$$CaO\ (s) + H_2O\ (l) \longrightarrow Ca(OH)_2\ (aq) \qquad (1)$$

Meanwhile, calcium hydroxide solution or limewater is produced with excess water followed by filtration. Eqn. (2) shows the formation of small particles of $CaCO_3$ with addition of carbon dioxide in $Ca(OH)_2$ [12].

$$Ca(OH)_2\ (aq) + CO_2\ (g) \longrightarrow CaCO_3\ (s) + H_2O\ (l) \qquad (2)$$

Calcium carbonate is unusual in that its solubility increases with decreasing temperature and increasing pressure. In this work, the sorption equilibria of CO_2 on synthesized CaO with presence of different amount of water were measured at 2°C, where hydrate is stable to form. The changes of surface morphology and chemical bonds in the samples before and after CO_2 adsorption was studied to verify the formation of CO_2 hydrates.

2 Methodology

2.1 Preparation of CaO from cockle shell

In this study, waste cockle shells were obtained from Seri Iskandar, Perak, Malaysia. Once received, the cockle shells were washed with water to remove dirt and oven dried at 110°C for 24 hrs to remove excess moisture. After that, the shells were crushed using pestle mortar and ground into powder by using an electrical grinder. Then the products were sieved for 10 minutes in the shaker sieve to ensure the powder was well segregated into various particle size fractions. The calcination process was carried out in tube furnace where 10 g of the powder was placed in ceramic sample boat and calcined at 850°C for 40 min in N_2 atmosphere [13].

2.2 Materials

The main chemicals used in the present work were de-ionized water and carbon dioxide (CO_2) for adsorption analysis. Helium (He) and compressed air were used as a carrier gas in HPVA II for degassing and purging processes. Mixture of glycol and water was used to provide the desired temperature for analysis process. Particle size of synthesized calcium oxide used in this research was < 0.1 mm. Ye *et al.* reported that less pore diffusion resistance is provided in smaller particle size and thus mass transfer of CO_2 through the sample core can be improved [14]. In addition, smaller particle size has wider surface area in which influence the adsorption capacity of the gas [15]. The specific surface area of the synthesized CaO is 8.79 m^2/g and the pore volume is 1.72 x 10^{-2} cm^3/g, which were determined from N_2 adsorption data at 77 K using Brunauer-Emmett-Teller (BET) equation.

2.3 Experimental work

The CO_2 sorption isotherms were measured by using a static volumetric method where the measurements were performed by using a static High Pressure Volumetric Analyzer (HPVA II) from Particulate System. In the present work, CO_2 sorption on synthesized CaO with presence of different amount water was measured at temperature of 2°C. Prior of CO_2 adsorption, 300- 400 mg samples were placed inside a 2 cm^3 sample chamber and inserted into a furnace for degassing process. A filter gasket of size 60 µm was placed on top of the sample chamber to prevent the fine samples from entering the valves. The samples were evacuated at temperatures of 200°C under a vacuum condition for overnight to remove any impurities retained inside the sample. Once the degassing process completed, the sample chamber was moved to analysis port for adsorption measurement. The adsorption was started by dosing CO_2 to the system and the valve between the loading and sample cell was opened to allow gas contacted with the samples. During adsorption, holding time for each pressure interval was set at 45 min to ensure equilibrium state was achieved [16]. Final equilibrium pressure and quantity of gas adsorbed was recorded when the sample reached equilibrium with CO_2. This process was repeated at a given pressure intervals until the maximum pre-selected pressure reached. Each of the resulting equilibrium points (volume adsorbed and equilibrium pressure) was then plotted to provide an isotherm. The amount of CO_2 adsorbed in the studied samples is expressed in mmol CO_2 on the basis of per gram of dry sample. While for CO_2 adsorption onto wet sample, the degassing process was skipped in order to avoid removal of water vapour from wet sample. Water content in a wet sample was expressed as Rw; the weight ratio of water to sample. Since each isotherm starts at a pressure reading of zero, it is necessary to place the system in a vacuum [17]. Thus, the wet sample was cooled to – 20°C for 4 h to minimize the loss of water due to vaporization [18]. Then, the temperature of the chamber was raised to the specified value before sorption measurement was started [5].

2.4 Material characterization

Material characterizations for the synthesized CaO before and after analysis were conducted in order to verify the formation of CO_2 hydrate onto the surface. A Perkin-Elmer Spectrum One Fourier Transform Infrared (FTIR) Spectroscopy was used to study the functional group exist on the calcium-based structure. The FTIR analysis was performed within the spectrum range 450 to 4000 cm^{-1}. The analysis involved mixing of 1% samples with the potassium bromide (KBr) and pressed the samples into pellet shape. Field Emission Scanning Electron Microscope (FESEM) was a method to visualize the surface structure of the samples. The analysis was performed by mounting the samples onto adhesive carbon tape attached to the aluminium platform. The electrons beam will be attracted to the atoms and creates patterns and images of the structure.

3 Results and discussions

3.1 CO_2 sorption on wet CaO at 2°C

The sorption isotherms of CO_2 in synthesized CaO with different amount of water were obtained at 2°C and shown in Fig. 1. The highest pressure is about 36 bar, at which CO_2 condensation occurs. The isotherm for dry CaO (curve 1) is relatively low as this type of process can be classified as chemisorption in which there is a reaction for CaO to adsorb CO_2. It is requires activation energy in which adsorption capacities is first increase with increasing of temperature. However, the isotherms on wet CaO are affected by the amount of water content in the samples. There is a significance improvement can be observed due to the remarkable changes in the sorbent's texture during the addition of some amount of water [19]. It is believed that the higher sorption amount is due to the higher solubility of water in CaO. Wang *et al.* [16] have reported that CaO particles will transform into small $Ca(OH)_2$ particles and a part of $Ca(OH)_2$ dissolves with the pore structure becoming loose. The isotherms with low values of Rw (curves 2, 3, 4 and 5) show an inflection pressure in which the sorbed amount increases to a higher level. The phenomenon was observed in porous material as water activity is depressed by partial ordering and bonding of water molecules with hydrophilic pore surfaces [20]. Basically, the inflection pressure is referred to hydrate formation pressure and indicates the beginning of hydrate formation [17]. Thus, the phenomenon is considered normal for porous material where the inflection pressures were observed higher than the formation pressure of CO_2 hydrate in pure water (15.7 bar at 2°C) [21]. From Fig. 1, it can be observed that the hydrate is started to form at pressure around 25 bar for curves 4 and the hydrate formation pressure increases for curves 2 and 3. The phenomenon may due to insufficient amount of pre-adsorbed water to trap CO_2 molecules for formation of CO_2 hydrate in which only the smaller pores are firstly filled with water [18]. When hydrate is formed in small pores, very high excess Gibbs free energies is produced on the surface and required higher formation pressure [18]. It is apparent that the lower CO_2 capture capacities by CaO are obtained when there too much water content (curves 6, 7 and 8) as illustrated in Fig. 1. The phenomenon was observed as excess water may limit the reaction due to the blockage of the pores in the solid [22]. Therefore, less amount of CO_2 can be adsorbed and its condensation may lead to more formation of $Ca(OH)_2$. Fig. 2 illustrated the effects of Rw on CO_2 sorption amount at 30 bar. The highest storage capacity (6.32 mmol/g) is reached for Rw = 0.55, which is about 30 times higher than dry CaO. It is clear that excessive water does not give a big impact on amount adsorbed, but an appropriate quantity of water added to CaO greatly enhances the CO_2 adsorption.

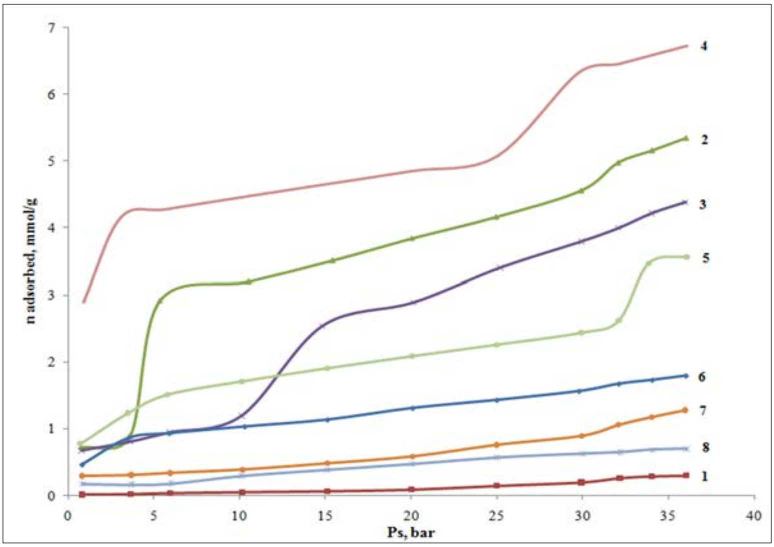


Figure 1: Sorption isotherms of CO_2 in synthesized CaO with different amount of water 1: Rw = 0; 2: Rw = 0.30; 3: Rw = 0.47; 4: Rw = 0.55; 5: Rw = 0.88; 6: Rw = 1.14; 7: Rw = 2.00; 8: Rw = 3.73.

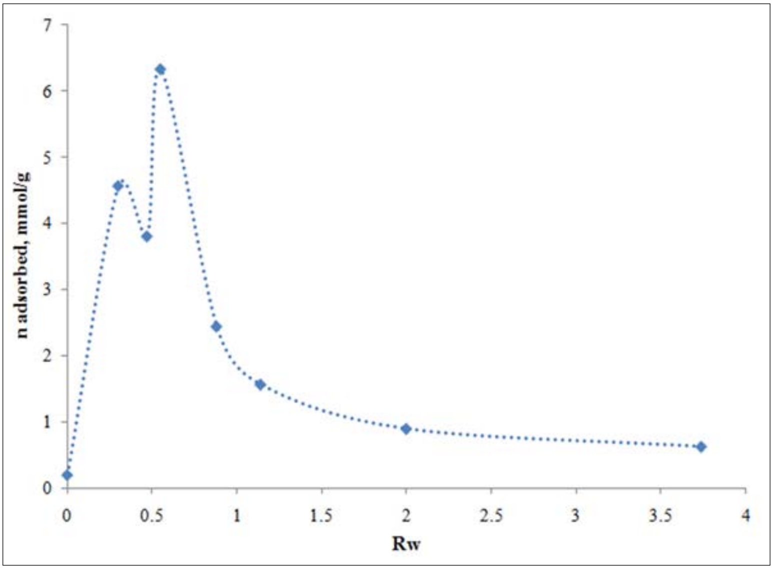


Figure 2: Effects of Rw on CO_2 sorption amount at 30 bar.

Table 1 shows the comparison of adsorption capacities and Rw values from this work with those values reported in literatures. Generally the CO_2 uptake was comparable with other porous materials but differ in Rw values. As reported by other studies, the sorption capacity increases with increasing of Rw value. However, opposite trend has been observed in this work due to type physical properties of the solid. From physisorption analysis, both samples use in this work have been classified as mesoporous material as the average pore diameters fall in the range of 20 to 500 Å. As CO_2 molecules has smaller molecular diameter which is 3.34 Å, the large pore width gives plenty of space in accommodating the molecules onto them. Thus, excessive of water will act as a trap for the penetrating water molecules, which are retrain within the pores. Besides, specific area and the pore volume are also the important characteristics where adsorption capacities of a solute are directly proportional to them [23]. Kang *et al.* [24] have measured the hydrate phase equilibria of binary CO_2 + water in porous silica gel and it is confirmed the total amount of sorbed water in the sample was almost identical to the pore volume of sample. Therefore, a small amount of pre-adsorbed water is required on CaO as pore volume of CaO is relatively small compared with other porous material.

Table 1: CO_2 sorption in other porous materials at 2°C.

Adsorbent	Sorption capacity (mmol/g)	Rw	Ref.
Activated carbon BY-1	31	1.65	[5]
Bamboo chips	12.1	2.36	[1]
Silica gel SG-A	2.5	0.75	[3]
Silica gel SG-B	2.7	0.81	[3]
Silica KIT-6	12.8	2.48	[18]
Synthesized CaO	5.07	0.55	This work

3.2 FTIR spectra analysis

The identification of chemical constituents in a compound can be obtained from the characteristic frequencies which provide the usefulness of qualitative analysis. FTIR spectroscopy is an important instrument used to identify different phases due to the differences in their carbonate ions, CO_3^{2-}. The IR spectra of raw cockle shell, synthesized CaO after and before CO_2 adsorption are shown in Fig. 3(a), (b) and (c); respectively. As illustrated in Fig. 3(a), there is a broad transmission band at approximately 3417.48 cm^{-1} in raw cockle shell spectra where it can be attributed to OH stretching vibration from residual water [25]. The weak bands at 1788.08 cm^{-1} corresponds to C=O bonds from carbonate [25]. The other functional group, represented by the smaller absorption bands in cockle shell was carboxylic acid which is at 2522.24 cm^{-1} [26]. The bending modes of calcium carbonate can be well defined by infrared band at 861.62 cm^{-1} [27]. The presence of aragonite in cockle shell can be further confirmed by a IR spectra at 1082.75 cm^{-1} of CO_3^{2-} symmetric stretching [26, 28, 29]. While the sharp band at 712.77 cm^{-1} is related to Ca-O bonds [29]. In the OH stretching vibration region, strong peak at 3642.22 cm^{-1} was observed in IR spectra of synthesized CaO (refer to Fig. 3(c)) due to intensity of surface OH band increase with increasing of temperature as compared with raw cockle shell [25, 29]. The two carbonate bands at ~ 700 cm^{-1} in aragonite were not extinction in Fig. 3(c) due to formation of CaO after calcination process. The wide band at 559 cm^{-1} corresponds to the Ca-O band [25]. The absorption peak of calcite at 875.79 cm^{-1} can be observed in synthesized CaO which indicates the presence of calcite after calcination process [26]. These changes observed in the spectrum of synthesized CaO indicated the possible involvement of those functional groups on the surface of the cockle shell during calcination process. The broad band at 1479.80 and 1471.80 cm^{-1} which are illustrated in Fig. 3(a) and (b); respectively can be attributed to the alkyl group which is present in the aragonite polymorphs [26]. Thus it is verified the formation of $CaCO_3$ after undergo CO_2 adsorption on wet CaO.

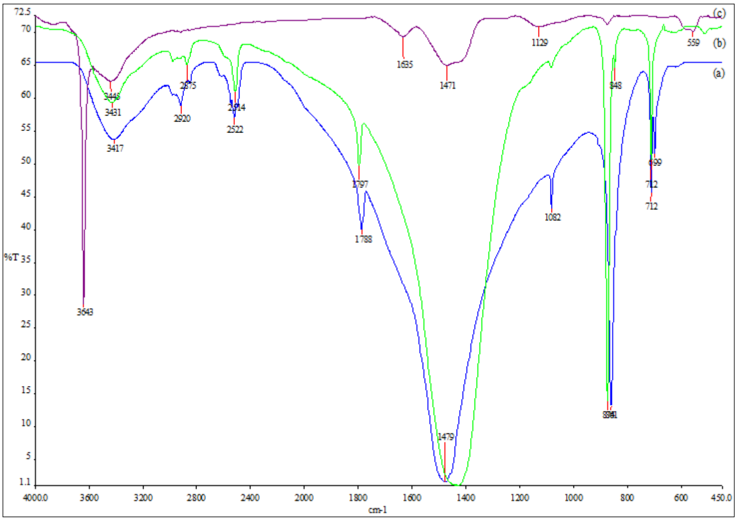
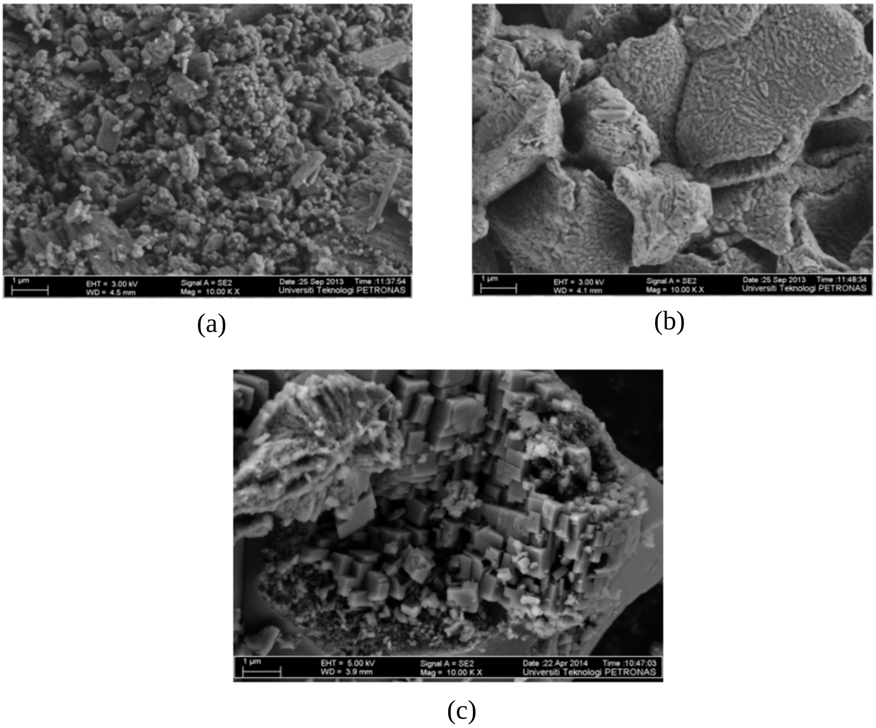


Figure 3: FTIR spectra of (a) raw cockle shell, (b) synthesized CaO after adsorption and (c) synthesized CaO.

3.3 Surface morphology

Theoretically, aragonite ($CaCO_3$) has a needle like structure while calcium oxide has more uniform, well distributed and sphere like structure [30]. Fig. 4(a) illustrates the structure of raw cockle shell. The natural occurrence of whisker structure of aragonite is due to biogenic origin and mineral organisms as reported by Wang and Thomson [31]. Contrary to raw cockle shell, synthesized CaO agglomerates are larger, rounded and profusely cracked as shown in Fig. 4(b) [32]. Sun *et al.* [33] claimed that the grain shape are almost spherical but with some evidence of initial grain-neck growth due to early stage of sintering. After CO_2 adsorption, incipient crystal face development can clearly been seen in Fig. 4(c) to indicate formation of gas hydrate.



(a) (b)

(c)

Figure 4: FESEM image of (a) raw cockle shell, (b) synthesized CaO and (c) wet CaO after CO_2 adsorption.

4 Conclusion

The remarkable difference was observed in the CO_2 sorption behaviour on synthesized CaO with presence of water. The highest enhancement of sorption capacity was obtained in wet sample with water loadings of Rw = 0.55, which is about 30 times sorption amount than that on dry sample. The formation of CO_2 hydrate has been further verified by FTIR spectra and surface morpholgy changes. Thus, it can be concluded that water can enhance amount of CO_2 adsorbed on synthesized CaO, in which it can be further utilized for controlling CO_2 emission.

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