Adsorption of mesoporous carbon modified with triethylenetetramine as a function of carbon dioxide flow time

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Abstract. We synthesize mesoporous carbon by using the soft-templated method with pluronic F-127 as a structure-directing agent, and phloroglucinol and formaldehyde as carbon precursors. The as-synthesized mesoporous carbon was characterized by using x-ray diffraction, Brunauer, Emmett and Teller (BET), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), and Fourier transform infrared (FTIR) spectroscopy. The as-synthesized mesoporous carbon was activated by using 1M HCl to increase the triethylenetetramine (TETA) as amine group compound loading within mesoporous carbon. Mesoporous carbon and activated mesoporous carbon was modified by using TETA with concentration variations less than 50 wt%. The modified mesoporous carbon was also characterized by using SEM-EDX and FTIR. Adsorption tests were done by using adsorbent mesoporous carbon, activated mesoporous carbon, mesoporous carbon modified by TETA, and activated mesoporous carbon modified by TETA with CO₂ gas flow times of 5, 10, 15, 20, 25, and 30 min, a contact time of 15 min, and a flow rate of 20 mL/min. The adsorbed CO₂ gas was quantified by using the acid–base titration method. On the basis of the CO₂ adsorption test, the acid activation was successfully increased by TETA loading within mesoporous carbon, which increases the ability of the material to adsorb CO₂.

1. Introduction

With increases in world population and industrialization, energy consumption has increased significantly over recent decades. Nearly 85% of the world’s energy comes from fossil fuels, which release tremendous quantities of CO₂ into the atmosphere. Over the last half century, research has shown that the concentration of CO₂ in the atmosphere has increased from 310 to 390 ppm [1]. Such an increase in CO₂, if it continues, will increase the average temperature of earth and lead to global climate change.

Carbon captures and storage (CCS) is an efficient method to reduce the emission of CO₂ into the atmosphere. CCS is a three-step process: separation of CO₂ from other emissions before entering the atmosphere, CO₂ transportation, and permanent storage of the CO₂. Available technologies for CO₂ capture include physical absorption, chemical absorption, adsorption, and membrane [2]. In physical absorption, CO₂ is adsorbed at high pressure and low temperature and is desorbed at low pressure and high temperature. The conditions for physical absorption are not suitable for CO₂ capture because the requisite pressure is relatively high. Chemical absorption using amine solution has been used in many industries to capture CO₂. Although this technology is highly efficient (98 %) [1], it corrodes the equipment, consumes significant regeneration energy, and requires a high amount of absorbent [2]. Therefore, using a solid material, such as activated carbon, zeolite, metal oxide, alumina, or mesoporous carbon, as adsorbent can overcome the drawbacks of chemical absorption [3].

Mesoporous carbon has high pore volume and surface area, is stable thermally and mechanically, is stable against strong acids and bases, is inert, and is an ordered mesoporous structure. As CO₂ adsorbent, mesoporous carbon has high adsorption capacity and adsorption affinity for CO₂ [4]. The
introduction of amine groups improves CO$_2$ adsorption efficiency and selectivity in the gas mixture. The use of amine groups within a solid adsorbent can reduce corrosive and toxic characteristics, as observed in absorption using amine solution.

Pamungkas [5] demonstrated that mesoporous carbon modified with 50 wt.% EDA has the best adsorption ability and leads to a higher concentration of amine groups, which close the pores, thus reducing the adsorption ability of this material. Faisal [6] and Sulistianti et al. [7] modified mesoporous carbon and activated carbon with TETA at concentrations below 50 wt.%. The adsorption tests show that modified mesoporous carbon with TETA increases the CO$_2$ adsorption ability. Conversely, modified activated carbon with TETA decreases the CO$_2$ adsorption ability.

In the present research, we synthesize mesoporous carbon by using the soft-templated method and activate it with acid. Mesoporous carbon and activated mesoporous carbon is then modified with TETA. We then compare the CO$_2$ adsorption ability of the different materials.

2. Experimental methods

2.1. Materials
The following materials were used: phloroglucinol, pluronic F-127, formaldehyde 37%, ethanol, chloride acid (HCl) 37%, triethylenetetramine (TETA), sodium hydroxide (NaOH) pellets, potassium hydrogen phthalate (KHP), borax (Na$_2$B$_4$O$_7$·10H$_2$O), indicator phenolphthalein, indicator methyl orange, indicator methyl red, CO$_2$ gas (99.99% UHP), N$_2$ gas (99.99% UHP), and deionized water.

2.2. Synthesis of mesoporous carbon
Mesoporous carbon was synthesized by mixing 1.25-g phloroglucinol and 1.25-g pluronic F-127 into a 9.7 g of a 10:9 w/w ethanol–water mixture. To the solution was added 0.08 mL of HCl 37 % (w/w) as a catalyst. Next, 1.25 mL of formaldehyde 37 % (w/w) solution was added. The hydrothermal process was then applied (100°C for 24 h). The resulting material was carbonized by using a tubular furnace under a stream of N$_2$ gas. The resulting mesoporous carbon was then characterized by using Fourier transform infrared (FTIR) spectroscopy, x-ray diffraction, scanning electron microscopy energy dispersive x-ray spectroscopy (SEM-EDX), and Brunauer-Emmett-Teller (BET) particle analytical.

Synthesized mesoporous carbon and activated mesoporous carbon were modified by impregnation with triethylenetetramine (TETA). The TETA-modified mesoporous carbon and activated mesoporous carbon were then characterized by using FTIR and SEM-EDX.

2.3. Application for adsorption carbon dioxide
The CO$_2$ adsorption test was performed in a reactor by streaming CO$_2$ and N$_2$ gas onto 0.2 g of adsorbent. The CO$_2$ not adsorbed is collected in 0.5-M NaOH solution and analyzed quantitatively by using the titrimetric method.

3. Results and discussion

3.1. Synthesis and characterization of mesoporous carbon
The mesoporous carbon was synthesized by using the soft-templated method with pluronic F127 as a template, and phloroglucinol and formaldehyde as carbon source [8]. The formation of monolith was followed by a hydrothermal process to decompose the template and form a porous structure. After the hydrothermal process, the mesoporous polymer was then carbonized under a stream of N$_2$ gas to decompose the polymer and increase the surface area of the mesoporous carbon.

3.2. X-ray diffraction
Figure 1a shows the x-ray diffraction pattern of synthesized mesoporous carbon. The x-ray diffraction pattern according to the JCPDS index, No. 75-1621, shows two distinctive peaks at 2θ around 22°–26° (002) and 42°–46° (101) [9]. The peaks at 2θ = 24.3° and 43.8° are from the diffraction planes of hexagonal graphitic carbon. The broad peaks indicate that the as-synthesized mesoporous carbon is amorphous.

The grazing-incidence x-ray diffraction pattern reveals a strong peak at 2θ ~1° as shown in figure 1b. This result is consistent with the x-ray diffraction pattern of as-synthesized mesoporous carbon by Liang and Dai [9], who found a sharp peak 2θ = 0° to 1° (100), which indicates a two-dimensional hexagonal symmetry [10].
3.3. FTIR spectra

The FTIR spectra of as-synthesized mesoporous carbon are shown in figure 2a, the spectrum of the material before carbonization shows the O–H stretching vibration at ~3500 cm$^{-1}$ from the O–H group in phloroglucinol and the symmetric and antisymmetric stretching vibration of the methylene group (CH$_2$) at ~2900 cm$^{-1}$, which occurs as a result of bonding between formaldehyde and phloroglucinol. After carbonization, the peaks corresponding to the O–H stretching vibration and the C–H stretching vibration disappear, which indicates that the carbonization process removes O and H atoms from the pre-carbonized mesoporous carbon, leaving a carbon material. This is because the carbonization process decomposes pluronic F127, phloroglucinol, and formaldehyde.

The FTIR spectra of activated mesoporous carbon (figure 2b) shows a wide absorption peak at 3200–3600 cm$^{-1}$, which corresponds to the O–H stretching vibration. Weak absorption at 1500–1640 cm$^{-1}$ corresponds to overlapping stretching vibrations of C=C and C=O. A weak vibration at 1000–1250 cm$^{-1}$, which is a C–O stretching vibration, indicates ether, hydroxyl, and phenolic structures [11].

The FTIR spectra of as-synthesized mesoporous carbon and activated mesoporous carbon modified by TETA have absorption peaks at 3100–3600 cm$^{-1}$ (figure 3a and figure 3b) which associate with N–H stretching vibrations, and absorption at 1580–1650 cm$^{-1}$, which associate with N–H bending vibrations.
Table 1. Elemental composition of mesoporous carbon, as synthesized, modified with TETA, and activated mesoporous carbon modified with TETA.

| Sample       | Mass percent (%) | Atomic percent (%) |
|--------------|------------------|--------------------|
|              | C    | N    | O    | C    | N    | O    |
| MC           | 89.73| 0.00 | 10.26|
| MC-TETA10    | 70.73| 18.66| 10.61|
| MC-TETA20    | 69.16| 17.20| 13.63|
| MC-TETA30    | 64.56| 23.04| 12.41|
| MC-TETA40    | 64.21| 23.22| 12.57|
| MC-TETA50    | 65.90| 20.81| 13.29|
| AMC-TETA10   | 68.38| 18.86| 12.76|
| AMC-TETA20   | 64.00| 20.75| 15.26|
| AMC-TETA30   | 76.77| 15.66| 7.57 |
| AMC-TETA40   | 63.57| 21.64| 14.78|
| AMC-TETA50   | 51.04| 26.63| 22.33|

Figure 3. FTIR spectra of mesoporous carbon modified with TETA (a) as-synthesized and (b) activated.

Figure 4. SEM images of as-synthesized mesoporous carbon with a magnification of (a) 3000×, (b) 7000×, and (c) 20000×.

3.4. Scanning electron microscopy and energy dispersive x-ray spectroscopy

SEM images of the sample with three different magnifications are shown in figure 4. The surface of as-synthesized mesoporous carbon has a smooth morphology near the holes in its surface. The surface of mesoporous carbon with holes indicates that this material is suitable as CO\textsubscript{2} adsorbent.

The measured elemental contents of the synthesized mesoporous carbon are carbon, nitrogen, and oxygen (see table 1). Carbon is the most abundant element in the as-synthesized mesoporous carbon, with an atomic percent of 89.74%, followed by oxygen with 10.26%. Mesoporous carbon and activated mesoporous carbon are both successfully modified with TETA, as indicated by the presence in both of elemental nitrogen.
3.5. Surface-area analysis
The adsorption isotherm curve in figure 5 shows that mesoporous carbon has type-IV adsorption–desorption isotherms, which indicates that the synthesized material is a mesoporous material. At relative pressures of about 0.45 to 0.85, a hysteresis loop appears that is a characteristic of mesoporous material. On the basis of the pore-size distribution curve, the pore diameter is 8.08 nm. On the basis of adsorption isotherm curve and the pore-size distribution curve, mesoporous material was successfully synthesized. The surface area, pore volume and diameter are listed in table 2.

3.6. Carbon dioxide adsorption test
Carbon dioxide adsorption tests were done on adsorbent mesoporous carbon, activated mesoporous carbon (figure 6a), mesoporous carbon modified with TETA, and activated mesoporous carbon modified with TETA (figure 6b). The amount of CO₂ gas adsorbed on mesoporous carbon is similar but slightly less than that adsorbed on activated mesoporous carbon. This result is attributed to the fact that the activated mesoporous carbon was washed and heated, which increases its surface area and

### Table 2. Analysis of surface area, pore volume, and pore diameter of mesoporous carbon.

| Sample          | Surface area (m²/g) | Pore volume (cm³/g) | Pore diameter (nm) |
|-----------------|---------------------|---------------------|--------------------|
| Mesoporous carbon | 416.2329           | 258.9194            | 157.3135           |
|                 | 0.1942              | 0.0657              | 8.08               |

### Figure 5. Adsorption–desorption isotherms for mesoporous carbon
- (a) Adsorption–desorption isotherms
- (b) Pore-size distribution curve of mesoporous carbon

### Figure 6. Carbon dioxide adsorption curve for mesoporous carbon
- (a) as-synthesized (blue, MC) and activated (red, AMC) and modified with TETA
- (b) as-synthesized (red, MC-TETA30) and activated (blue, AMC-TETA30)

Figure 5.
- (a) Adsorption–desorption isotherms for mesoporous carbon
- (b) Pore-size distribution curve of mesoporous carbon.

Figure 6.
- (a) Carbon dioxide adsorption curve for mesoporous carbon
- (b) Carbon dioxide adsorption curve for mesoporous carbon
Figure 7. Cumulative carbon dioxide adsorption for mesoporous carbon (a) as-synthesized (blue, MC), activated (green, AMC), modified with TETA (red, MC-TETA30), and activated and modified with TETA (cyan, AMC-TETA30).

pore volume. Modification of mesoporous carbon and activated mesoporous carbon with TETA increases CO\textsubscript{2} adsorption. On the basis of the data obtained, the activated mesoporous carbon modified with 30% TETA and the mesoporous carbon modified with 30% TETA adsorb CO\textsubscript{2} gas at a rate of 117.7096 and 111.2263 mmol/g adsorbent, as shown in figure 7. This result indicates that the activation of mesoporous carbon successfully increases amine loading within the mesoporous carbon, which also increases its ability to adsorb CO\textsubscript{2}. The best material for adsorbing CO\textsubscript{2} is thus activated mesoporous carbon modified with 30% TETA (117.7096 mmol/g adsorbent).

4. Conclusions

Studies of CO\textsubscript{2} adsorption onto carbon-based adsorbents show that the amounts of adsorbed CO\textsubscript{2} increase with increasing CO\textsubscript{2} flow time. Acid activation of as-synthesized mesoporous carbon increases amine loading within mesoporous carbon, thus increasing the CO\textsubscript{2} adsorption ability of activated mesoporous carbon modified with amine.

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References

[1] Liu Y, Wang Z U and Zhou H C 2012 Greenh. Gases: Sci. Technol. 2 239–59
[2] Yu C H, Huang C H and Tan C S 2012 Aerosol Air. Qual. Res 12 745–69
[3] Wang J, Chen H, Zhou H, Liu X, Qiao W, Long D and Ling L 2013 J. Environ. Sci. (China) 25 124–32
[4] Zhou L, Liu X, Li J, Wang N, Wang Z and Zhou Y 2005 Chem. Phys. Lett. 413 6–9
[5] Pamungkas A Z 2014 Synthesis of Mesoporous Carbon Modified by Amine Groups as Carbon Dioxide Adsorbent (Depok: Universitas Indonesia) Undergraduate Thesis
[6] Faisal M 2015 Study of The Effect of Modified Triethylentetramine on Mesoporous Carbon on The Absorption of CO\textsubscript{2} Gas (Depok: Universitas Indonesia) Undergraduate Thesis
[7] Sulistianti I, Krisnandi Y K and Moenandar I 2017 IOP Conf. Ser.: Mater. Sci. Eng. 188 012041
[8] Görka J, Zawislak A, Choma J and Jaroniec M 2010 Appl. Surf. Sci. 256 5187–90
[9] Liang C and Dai S 2006 J. Am. Chem. Soc. 128 5316–7
[10] Libbrecht W, Deruyck F, Poelman H, Verberckmoes A, Thybaut J, de Clercq J and van der Voort P 2015 Chem. Eng. J. 259 126–34
[11] Park S J and Jang Y S 2002 J. Colloid Interface Sci. 249 458–63