Study of CO₂ adsorption capacity of mesoporous carbon and activated carbon modified by triethylenetetramine (TETA)

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Abstract. Mesoporous carbon was synthesized by soft template method using phloroglucinol and formaldehyde as a carbon source; and Pluronic F-127 as a mesoporous template. The synthesized mesoporous carbon and commercial activated carbon were modified with triethylenetetramine (TETA) to increase CO₂ adsorption capacity. Based on FTIR characterization, the synthesized mesoporous carbon and the activated carbon without modification process has similarity pattern. After the modification, both of them showed absorption peaks in the area around 1580 to 1650 cm⁻¹ which is known as N-H bending vibration and absorption peaks in the area around 3150 to 3380 cm⁻¹ which is known as N-H stretching vibration. The XRD results showed two peaks at 2θ = 24.21° and 2θ = 43.85°, according to JCPDS index No. 75-1621 those peak are the typical peaks for hexagonal graphite carbon. In BET analysis, the synthesized mesoporous carbon and activated carbon modified TETA have surface area, pore volume and pore diameter lower than without modification process. In carbon dioxide adsorption testing, the synthesized mesoporous carbon showed better performance than the commercial activated carbon for CO₂ adsorption both without modification and by modification. The synthesized mesoporous carbon obtained CO₂ adsorption of 9.916 mmol/g and the activated carbon of 3.84 mmol/g for on 3.5 hours of adsorption. It is three times better than activated carbon for adsorption of carbon dioxide. The modified mesoporous carbon has the best performance for adsorption of gas CO₂ if compared by unmodified.

1. Introduction

The industrial revolution was the starting point for environmental issues such as greenhouse effect that leads to global warming. The industrial revolution is an increase in resource utilization will increase industrial activity. Carbon dioxide (CO₂) acts as a blanket to trap infrared radiation coming from the earth's atmosphere, causing warming of the earth and the temperature increase [1].

Carbon Dioxide Capture and Storage (CCS) can stop global warming through the reduction of greenhouse gas emissions, mainly capture process [2]. Absorption amine is advanced commercial technology to remove CO₂ [3]. However, this method is toxic, causing corrosion of equipment, and requires high energy for solvent regeneration. Therefore developed physical adsorption of CO₂ using a solid adsorbent such as zeolite, a metal-organic, porous silica, clay incandescent, and a carbon material such as activated carbon. The adsorption process does not cause corrosion of equipment and environmental pollution, but has the lower capacity of CO₂ adsorption at high temperatures [3].

To search for a suitable adsorbent developed mesoporous materials such as mesoporous carbon material for the adsorption of CO₂ because it has a high porosity, have large pores, have a large surface area, have a good design for pore structure, and requires low energy. Amine functional groups
such as Triethylenetetramine (TETA) is introduced to make it easier to interact with CO$_2$ [3]. Amine group adsorbs CO$_2$ and reversibly react with CO$_2$ to form carbamates and bicarbonate. Adsorbent modified amine is a promising way to capture the CO$_2$ because it has a high adsorption selectivity and the diffusion rate of CO$_2$ in high mesoporous.

Pamungkas [4] have successfully demonstrated that mesoporous carbon modified with 50 wt.% EDA has the best CO$_2$ adsorption capability for more amine groups which can cover the mesoporous carbon pores thus blocking the adsorption of CO$_2$. Faisal [5] have successfully demonstrated that mesoporous carbon modified with 30 wt.% TETA has the best adsorption capability and comparing the ability of the mesoporous carbon adsorption and activated carbon for the adsorption of CO$_2$ gas.

This research will be conducted synthesis of mesoporous carbon with soft-template method are then modified amine groups by impregnation method. Then will be compared to commercial activated carbon adsorption ability to CO$_2$.

2. Materials and methods

2.1. Materials
The materials used were Activated Carbon from Bratachem, Phloroglucinol, Pluronic F-127, Formaldehyde 37%, Ethanol, Chloride Acid (HCl) 37%, Triethylenetetramine (TETA), Sodium Hydroxide (NaOH) pellet, 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
Synthesis of mesoporous carbon was prepared by mixing 1.25 g phloroglucinol and 1.25 g Pluronic F-127 into the ethanol-water mixture 10:9 (w/w) of 9.7 g. The solution was added 0.08 mL of HCl 37% (w/w) as a catalyst. After that 1.25 mL of formaldehyde 37% (w/w) solution was added. Then do the hydrothermal process at a temperature of 100°C for 24 hours. The resulting material is carbonized with a tubular furnace under the stream of N$_2$ gas. Synthesized mesoporous carbon is then characterized using FTIR, XRD, SEM, and BET.

Synthesized mesoporous carbon and activated carbon was modification with Triethylenetetramine (TETA) by impregnation method. Mesoporous carbon and activated carbon modified TETA characterized by a FTIR and BET.

2.3. Application for adsorption carbon dioxide (CO$_2$)
Test adsorption of carbon dioxide (CO$_2$) is performed in a reactor by stream of CO$_2$ and N$_2$ gas to 0.2 g adsorbent. Then the CO$_2$ does not adsorbed is collected in 0.1 M NaOH solution and analyzed quantitatively by titrimetric method.

3. Results and discussion

3.1. Synthesis and characterization of mesoporous carbon
The mesoporous carbon were synthesized by soft-template method through hydrothermal treatment using copolymer Pluronic F-127 as a mesoporous template; using phloroglucinol and formaldehyde as a carbon source [6]. The hydrothermal process aims to form a pore structure, which is the decomposition of template. After hydrothermal process, the mesoporous polymer will be formed subsequently carbonized to polymer decomposition and increase the surface area of the synthesized mesoporous carbon [7].

3.2. X-Ray diffraction (XRD)
X-ray diffraction pattern of carbon material according to JCPDS index, No. 75-1621, that there are two distinctive peaks at 2θ area around 22-26° and 42-46° [8]. Two peaks at 2θ = 24.21° and 2θ = 43.85°
are diffraction planes of hexagonal graphitic carbon [9]. A broad peak indicates that the mesoporous carbon synthesized contains amorphous carbon (figure 1).

3.3. Fourier transform infrared (FTIR)
The FTIR spectrum carbon mesoporous synthesis product before carbonization (figure 2a) shows the absorption peaks at wave numbers around 3500 cm\(^{-1}\) which is the peak of the vibration of OH stretching phloroglucinol and absorption peaks at wave number 2900 cm\(^{-1}\) which is the absorption peak of the vibration of symmetric and asymmetric methylene group (CH\(_2\)). The FTIR spectrum synthesized mesoporous carbon after carbonization (figure 2a) indicates the absence of absorption peak at wave number around 3500 cm\(^{-1}\) and 2900 cm\(^{-1}\) which is an absorption peak of O-H stretching vibration and the vibration of symmetric and asymmetric methylene. This indicates that the mesoporous carbon have been synthesized because there are happened a decomposition of Pluronic F-127, phloroglucinol and formaldehyde.

The FTIR spectrum of activated carbon (figure 2b) has similarities with the FTIR spectrum synthesized mesoporous carbon. This indicated that both have the same functional groups. After modified by TETA appears absorption peaks in the area around 1580-1650 cm\(^{-1}\) which is N-H bending
vibration of TETA and absorption peaks in the area around 3150-3380 cm$^{-1}$ which is N-H stretching vibration of TETA (figure 2b).

3.4. Scanning electron microscopy (SEM)
Analysis by Scanning Electron Microscopy (SEM) was used to determine the size and morphology of carbon materials synthesis product. Synthesized mesoporous carbon surface morphology is smooth (smooth), by holes in its surface (figure 3). Surface with holes like this are very support to be used as an adsorbent gas carbon dioxide (CO$_2$).

3.5. Surface area analysis
Modifications by TETA does not change the structure of mesoporous carbon mesoporous (figure 4a). In figure 4a it is shown that the mesoporous carbon without modification and by modification of 10% TETA has adsorption-desorption isotherms curve similar (adsorption-desorption isotherms type IV) [10]. The difference is that the mesoporous carbon has a larger volume than mesoporous carbon modified TETA. This shows that modifications by TETA decrease the pore volume and decrease surface area (table 1). Figure 4b shows that the mesoporous carbon and mesoporous carbon modified TETA had a similar BJH desorption pattern. It is explained that the mesoporous carbon and mesoporous carbon modified TETA has similar a pore size distribution.

Based on the data, mesoporous carbon has the CO$_2$ adsorption capability better than activated carbon (figure 5a). Mesoporous carbon was able adsorbed CO$_2$ as much as 9.916 mmol/g adsorbent and activated carbon was able adsorbed CO$_2$ as much as 3.84 mmol/g adsorbent. It is very possible
Table 1. Surface area analyses of MC and MC-TETA 10% calculated from BET measurement.

| Sample        | S_{BET}^a (m^2/g) | S_{ext}^b (m^2/g) | V_{total}^c (cm^3/g) | V_{micro}^b (cm^3/g) | D_{pore}^d (nm) |
|---------------|-------------------|-------------------|----------------------|----------------------|-----------------|
| MC            | 407.278           | 337.622           | 0.6355               | 0.036                | 6.2409          |
| MC-TETA 10%   | 205.559           | 205.559           | 0.4149               | 0                    | 6.5691          |

Figure 5. (a) Curve of adsorption CO$_2$ by mesoporous carbon and activated carbon and (b) curve of adsorption CO$_2$ by mesoporous carbon, mesoporous carbon modified TETA, activated carbon and activated carbon modified TETA.

because mesoporous carbon’s pore is more uniform than activated carbon. In addition, the activated carbon dominated of micropores, thus activated carbon will be saturated more quickly than the mesoporous carbon. Modifications by TETA able to increase the ability CO$_2$ adsorption (figure 5b). Mesoporous carbon modified TETA was able adsorbed CO$_2$ as much as 10.932 mmol/g adsorbent and activated carbon modified TETA was able adsorbed CO$_2$ as much as 4.816 mmol/g adsorbent.

4. Conclusions
Adsorbent from mesoporous carbon and activated carbon have been prepared and their adsorption capacities were tested. The result showed that adsorption capacity of mesoporous carbon (9.916 mmol/g adsorbent) was better if compared with activated carbon (3.84 mmol/g adsorbent) and modification by 10% TETA could increase CO$_2$ adsorption capacity.

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