Crystallite structure of Palm shell Activated Carbon/MgO and Its Influence on Carbon Monoxide and Carbon Dioxide Adsorption

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Abstract. Gas emission of the motor vehicle is a major contributor to climate change, with a total of 14% emission annually, and the best potential option for reducing pollution is using the adsorption method. Magnesium oxide (MgO) has been proven as an effective adsorbent for liquid and gases. The impregnation of MgO on porous structure increases the affinity toward nonpolar gases, which is one of the purposes of this study. The crystallite structure is also a key factor that determines the adsorption capacity of activated carbon (AC). However, deeper analysis is needed in the activated carbon crystallite structure represented by d002 (aromatic layer), Lc (crystallite height), and La (crystallite diameter) on the adsorption of motor vehicle gas emissions. Three types of palm shell-based activated carbon were tested in this experiment. The results showed that activated carbon made using the two-step method and the AC/MgO produced surface structure with a d002 value of 0.33 nm and 0.32 nm, respectively. The impregnation of MgO on AC showed changes in surface structure and affected its crystallinity. The ability to adsorb CO2 and CO by AC/MgO increase up to 80% and 88%, respectively.

1. Introduction
Indonesia is one of the countries with the highest percentage of air pollution in the world. Indonesia's automobile growth has now increased by more than 10 percent every year, becoming a dominant factor in air pollution. Vehicles produce dangerous gases such as carbon monoxide (CO) and carbon dioxide (CO2). CO2 gas, in particular, is a major factor in global warming. To avoid extreme climate change, carbon dioxide emissions should be reduced from 2050 cases to 41-72% worldwide. Therefore, it is necessary to control environmental pollution. One of the ways that to reduce pollutants in the air is the use of biomass waste as a material that can be converted into activated carbon.

Palm shell's solid waste has a high quantity, which is around 9% per base 1 tons of palm fresh fruit bunches (FFB). So, there are 4.27 tons of biomass waste of palm shells per year. Previous research has shown that the palm kernel shell used as a raw material can produce activated carbon with a good surface structure with well-formed pores. The microporosity of activated carbon is highly dependent on its microstructure, especially from the structure of the aromatic layer. The common method to analyze the crystalline structure of activated carbon is using XRD. XRD has advantages such as providing information and the quantitative value of the carbon structure with a wide range [1]. Crystal structure parameters such as aromatic layer distance (d002), crystal height (Lc), and crystal diameter (La) are used for carbon structure analysis [2]. These three parameters have been proven valid and have also been used since the beginning of carbon structure research [3].
Another thing that can be used for improving the crystalline structure is metal oxide impregnation to activated carbon. Metal oxides such as MgO, TiO$_2$, BaO, CuO, and NiO have proven improving pore structure and shape. Modification of activated carbon with CuO can increase the surface area of BET to 658 m$^2$/g with a ratio of 1:1.5 [4]. MgO is also proven to have the ability to adsorb up to 43% CO gas [5]. Modification with NiO can increase the total pore volume from 12% to 41% [6]. The addition of metal will increase the active core so that the surface structure of the carbon changes and the surface area and absorption capacity of activated carbon will increase. 

Through this research, it is expected that metal oxide impregnation in activated carbon from palm oil shells can change its structure and become an alternative solution to increase the absorption capacity of motor vehicle gas emissions as an effort to improve air quality.

2. Experimental

2.1 Materials

There are three types of activated carbon used in this research. Two types of AC were made in the previous research, i.e., two step carbon (TSC) and one step carbon (OSC). The specifications can be seen in Table 1.

| Types | Iodine number (mg/g) |
|-------|----------------------|
| OSC   | 584.48               |
| TSC   | 1168.96              |

2.2 AC/MgO Synthesis

For the MgO modification, the TSC types were used. The steps for AC/MgO synthesis are described below:

a. Dissolve 0.5 grams of MgO in 50 ml of distilled water to make a 1% w/v solution.

b. Put 50 grams of activated carbon into the MgO solution so that the ratio of activated carbon to MgO is 1:1.

c. Stir the mixture of activated carbon and solution for 6 hours using a hot plate stirrer then let the solution stand for 18 hours at room temperature.

d. Filter the modified activated carbon using filter paper and dry the modified activated carbon using an oven at a temperature of 110 °C for 1 hour.

e. Carry out the reactivation process of modified activated carbon using a reactor by adjusting the reactor temperature at a of 550 °C with a flow rate of N$_2$ 175 ml/min for one hour.

f. Remove the modified activated carbon from the reactor, put it in a closed sample container, and store it in a desiccator.

The modified activated carbon (later was mentioned as TSC-M) was tested using iodine number ASTM D4607-94 and also all the AC types were characterized using X-Ray Diffraction (XRD) which determine the crystal structure, lattice parameters, and also the quantitative analysis.

2.3 Adsorption of CO and CO$_2$

The CO$_2$ and CO adsorption testing on motor vehicle emissions were carried out using a gas analyzer type AGS 688. The testing process refers to SNI 19-7118.3-2005 for type L motor vehicles. The test was done at normal temperature and atmospheric pressure. The scheme for adsorption process can be seen in figure 1.

Furthermore, the percentage of motor vehicle emissions that had been adsorbed was calculated based on the difference between the initial gas emission levels and the gas emission levels in the nth minutes as shown in equation 1.

\[
\% Adsorption = \frac{C_0 - C_n}{C_0} \times 100\%
\] (1)
Where:

\[ G_0 = \text{initial gas emission level (\% or ppm)} \]
\[ G_n = \text{level of gas emission in the } n^{th} \text{ minute (\% or ppm)} \]

3. Results and discussion

The activated carbon of the TSC type was modified by using MgO. MgO has been recognized as a type of oxide that can be used as an adsorbent with good adsorption ability. The addition of MgO to AC can increase contact with the active core, thereby improve its performance [7]. Different from other types of adsorbents, water vapor in the adsorbate gas mixture can be beneficial for the CO\(_2\) gas adsorption process by MgO [8].

The TSC-M was tested using iodine number to predict the surface area. The iodine number of TSC-M is 1005.31 mg/g. The TSC-M has a lower iodine number compared to the two other types of activated carbon because MgO has filled micropores in carbon and increased its microporosity [9]. Because of this, the iodine number decreases, indicating a reduction in the surface area of the AC.

The three types of AC were then characterized using XRD. The peaks from XRD can be seen in Table 2.

| Types  | kc  | \(\lambda\) | 2θ peak (°) | FWHM (nm) |
|--------|-----|-------------|-------------|-----------|
| OSC    | 0.94| 1.54        | 24.13       | 0.30      |
|        | 0.94| 1.54        | 29.98       | 0.19      |
|        | 0.94| 1.54        | 31.23       | 0.50      |
| TSC    | 0.94| 1.54        | 26.63       | 0.13      |
|        | 0.94| 1.54        | 29.07       | 0.56      |
|        | 0.94| 1.54        | 42.79       | 0.21      |
| TSC-M  | 0.94| 1.54        | 23.35       | 0.09      |
|        | 0.94| 1.54        | 42.67       | 1.19      |
|        | 0.94| 1.54        | 61.90       | 1.91      |

The XRD test results were then processed using the Origin Pro 8.5 (OriginLab Corporation) Software. The average crystallite size was calculated from the peak with the highest intensity in the XRD pattern using the Scherrer equation [10]. Then the calculation of the cryptic parameter is carried out with the Bragg Equation which is a derivative of the Scherrer equation. The diffraction angle 2θ and FWHM value for the two planes (002 and 100) were obtained by the curve fitting method. From these datas, calculations were made which include critical lattice parameters such as \(d_{002}\) (aromatic layer), crystallite height (Lc), crystallite diameter (La), and the number of aromatic layers per carbon crystallite (\(N_{ave}\)) using the Bragg equation. The calculation results showed in Table 3.
Table 3. Calculation of crystallite parameters

| AC types | 2θ_{002} | 2θ_{100} | FWHM{002} | FWHM{100} | d_{002} (nm) | Lc (nm) | La (nm) | N_{ave} |
|----------|-----------|-----------|------------|------------|--------------|---------|---------|--------|
| OSC      | 24.13     | 44.38     | 0.30       | 0.72       | 0.37         | 27.97  | 12.45   | 76.91  |
| TSC      | 26.63     | 42.79     | 0.13       | 0.21       | 0.33         | 66.96  | 42.56   | 201.18 |
| TSC-M    | 23.35     | 42.67     | 0.09       | 1.19       | 0.32         | 96.26  | 7.51    | 253.93 |

Commonly the d_{002} value ranges from 0.34 nm. The d_{002} values of the OSC and TSC-M samples were slightly above the literature. This can be due to the irregular structure between layers [11]. The second type of activated carbon, TSC, has a value of d_{002} which indicates that the TSC sample has a crystallinity level comparable to graphite [12]. The decreasing d_{002} value indicates the distance between the grains decreases, thus indicating an increase in the crystallinity of activated carbon.

From the adsorption test results, it can be seen that a significant increase in adsorption showed in the three types of AC. But modified activated carbon gives the best results, which can reduce CO₂ gas emissions by up to 80%. The data is reflected in figure 2.

![Figure 2. CO₂ Adsorption test result](image)

The adsorption capacity increases with increasing surface area of activated carbon. But in modified activated carbon, there is an increase in adsorption capacity even though the surface area decreases. This is caused by MgO which adds to the active site of the adsorbent. So, it can be concluded that the ability of CO₂ adsorption using activated carbon does not depend on the surface area, but rather on the porosity and crystallinity of activated carbon [2]. The crystallinity of AC can be defined with the lattice parameters mentioned before.

The adsorption process on activated carbon is predominantly physical adsorption. MgO supported by activated carbon increases the dipole ion interaction between MgO and CO₂. So that the texture properties and surface chemical properties affect the CO₂ adsorption performance [13]. The carbon will bind to the CO₂ molecule which is influenced by Van der Waals forces. If the adsorption process on activated carbon is generally physical adsorption, then the difference occurs in the CO₂ adsorption process on MgO. Several studies have shown that adsorption on MgO is more suitable using the pseudo-second-order model wherein this model chemical adsorption is more dominant. The results of the analysis using FTIR show that CO₂ adsorption on MgO is dominated by chemical adsorption with little physical adsorption [8].
The addition of MgO to activated carbon increases the polarity of the TSC-M sample so that this type will be good for binding nonpolar CO₂ gas. The chemical reaction between MgO and CO₂ can produce several bonds including unindents, bidentate carbonate, and bicarbonate types. Analysis conducted on literature resulted in the conclusion that the majority of compounds formed as a result of the reaction between CO₂ and MgO are types of bidentate carbonate. MgO helps the formation of hydroxyl radical compounds that are suitable for the adsorption of gases with non-polar properties [14].

In the adsorption process using TSC-M carbon, there is contact with two surfaces, the metal oxide surface, and the activated carbon. When the CO₂ molecule comes into contact with the metal oxide surface, there will be a direct carbonation process which is thermodynamically stable at ambient temperature and pressure conditions [15]. Also, the insertion of MgO increases the affinity for CO₂ [13]. MgO can adsorb CO₂ gas at room temperature which is good and proven to be effective. Based on the rate-limiting model, the CO₂ adsorption process on MgO is controlled by two things, film diffusion, and intraparticle diffusion. At the beginning of the adsorption process, the resistance from the diffusion of the film will regulate the adsorption rate. Then proceed with intraparticle diffusion resistance which is the main factor in the subsequent adsorption rate [8].

When the CO gas flow starts to hit the AC surface, the CO molecules will be adsorbed on the outer surface of the adsorbent at low pressure and gradually enter the inside of the adsorbent. In general, an increase in temperature will increase the ability of AC to adsorb CO gas. So, at standard pressure, CO gas is only adsorbed in the outer of adsorbent [16]. The results for CO adsorption showed in figure 3.

![Figure 3. CO adsorption result](image)

From this study, it is understood that the ability of activated carbon to adsorb CO₂ is better than CO, although the adsorption percentage of CO gas is higher because the initial content of CO gas in motor vehicle emissions is not as high as CO₂ gas. Simulations conducted by Lithoxoos show that the best ability of activated carbon to adsorb several types of gases is CO₂, CH₄, then CO, respectively [17]. One of the factors found prominent was the density profile of each adsorbate molecule. The density profile simulation results show that the majority of the adsorbed gas molecules are distributed near the pore walls. Besides, CO gas diffuses faster at high temperatures when CO₂ gas can diffuse more rapidly at room temperatures.

Based on the XRD results, the TSC-M carbon type has the smallest crystal size compared to other types. The small crystal size makes intraparticle diffusion more even. So, this shows that the crystallinity of carbon affects the adsorption of CO₂ and CO gases. The N₅₀ value of TSC-M is the highest among others and showed the best performances for adsorption. Also, the crystallite height
(Lc) proportional to the Nave value. This correlation might affect the adsorption process. But these matters are not certain yet and more research are needed for deeper analysis.

Carbon material plays an important key to improving environmental quality and also useful for other needs. Making activated carbon by paying attention to the crystallinity structure is one thing that can be done to get activated carbon that suits your needs. Good crystallinity of carbon can improve the quality of activated carbon so that this material is a promising material in the future.

4. Conclusion
In this paper, the structure of modified activated carbon was analyzed using X-ray Diffraction (XRD) method. MgO modified activated carbon (TSC-M) has the best adsorption of CO₂ and CO in motor vehicle emissions up to 80% and 88%, respectively, compared to the other AC types. The increase of aromatic layer and crystallite height are affecting the AC adsorption ability.

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