Synthesis and characterization of soft and hard templated mesoporous carbon using phloroglucinol as carbon precursor

I Amelia, Y K Krisnandi and I Abdullah

Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia

Corresponding author’s email: iman.abdullah@sci.ui.ac.id

Abstract. In this study, both soft and hard templated mesoporous carbon (ST MC and HT MC) were synthesized using phloroglucinol as carbon precursor. The templates used in soft and hard templated MC synthesis were Pluronic 127 (F-127) and SiO₂, respectively. The resulting mesoporous carbon were then impregnated with Ni and characterized using FTIR, SEM-EDS, BET, and XRD to investigate the functional groups, surface morphology, chemical composition, pore character, and crystallinity of the materials. The resulting Ni/MC was then utilized as a catalyst in transformation of CO₂ via carboxylation of phenylacetylene. The catalytic reactions were conducted with a variety of contact time (2, 4, 6 and 8 h) to obtain a reaction condition with the highest yield of phenyl propiolic acid. The resulting final product was tested using HPLC instrument. The phenyl propiolic acid showed best peaks at reaction time of 6 h for ST Ni MC catalyst with the area of 301 mAU and yield of 1.4 %. Meanwhile, HT Ni/MC catalyst showed the best performance in phenyl propiolic acid formation at the reaction time of 8 h with the area of 453 mAU and yield of 2.2 %.

Keywords: Mesoporous carbon, soft template, hard template, phloroglucinol, carboxylation.

1. Introduction

Carbon dioxide is a greenhouse gas that is suspected to be the main cause of global warming. The atmospheric concentration of carbon dioxide (CO₂) has been dramatically raised in the last decades as a result of the industrial development [1]. In 2015, it was recorded that CO₂ emissions from the energy sector in Indonesia reached 261.89 million tons [2]. So, the CO₂ control in the atmosphere needs to be conducted. Currently, there are two main strategies for reducing the CO₂ concentrations, namely: CO₂ capture and storage/sequestration (CCS) and CO₂ capture and its utilization (CCU). CCS is conducted by absorbing CO₂ using various absorbents such as solids, liquids, and membranes, then stored the CO₂ in a closed facility after desorption. While in the CCU strategy, the absorbed CO₂ is used as the raw material of value-added chemical compounds that make the system suitable for the chemical transformation of CO₂ at low pressure (ideally 1 atm), hence no stage of desorption [3]. The CCU’s strategy for the study centers on phenylacetylene carboxylation with CO₂ to produce carboxylic acid and its derivatives. However, it has a big challenge since CO₂ is highly oxidized and thermodinamically stable gas [1]. In fact, most of the reactions concerning CO₂ involve the application of large amount of stoichometric catalysts and a drastic reaction condition (high reaction temperature and/or high CO₂ pressure). Therefore, the renewable catalytic reactions development is indispensable for the chemical transformation of CO₂ [4]. Due to its stable nature, CO₂ requires low-valence metal assistance e.g. Ni(0)
or Pd(0) to react [5]. Among the transition metals, Ni has its own different uniqueness, such as relatively low-cost, its high activity, and its abundant in nature. Therefore, Ni has the potential as an alternative for precious metal catalysts. Nowadays it has been a lot of conversion of carbon dioxide by using the help of a homogeneous catalyst that is in an efficient reaction [3]. However, this homogeneous catalyst is difficult to be separated from the resulting product due to it has the same phase, making it takes a post-treatment. Therefore, the CO2 transformation method is developed using a heterogeneous catalyst so that the resulting product can be separated more easily and the catalyst can be reused for repeated reactions. On the other hand, mesoporous carbon (MC) has large surface area, pore size, ordered pore structure, and thermal stability [6]. For those reasons, MC has the potential to be used in CCU technology as catalyst support when combined with Ni metal. There are two types of MC synthesis: soft templated and hard templated. Soft templated MC is easier to synthesize while hard templated one has a more ordered structure. In this research, soft templated and hard templated MC were synthesized from phloroglucinol. Phloroglucinol and formaldehyde are able to polymerize via self-assembly around Pluronic F-127 micelle. The resulting polymer is also able to maintain its form during the degradation process, making phloroglucinol suitable as a precursor in the synthesis of mesoporous carbon [7]. The resulting MC was then utilized as a support material for Ni metal by impregnation. The objectives of the present study were to develop a high surface area templated carbon by pyrolysis of phloroglucinol carbon source in nitrogen environment using both soft and hard templated methods and its application as Ni catalyst support on carboxylation of phenylacetylene with CO2. The detailed effects of both methods on the development of porous carbon structure were studied. The properties of the precursors and template carbons were studied by Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray (EDX) and surface area and pore analysis.

2. Materials and method

2.1. Material

Hydrochloric acid (HCl) (37 % v/v) was procured from PT. Smart Lab Indonesia (Jakarta). Silica gel 60, formaldehyde (37 % v/v), N,N-dimethylformamide (DMF), and ethanol (99 % v/v) were purchased from Merck (Germany). Phloroglucinol, Pluronic F127, nickel (II) nitrate, magnesium bromide, phenylacetylene, and zinc powder were provided by Sigma Aldrich, aquadest was purchased from CV Satya Darmawan. Hydrogen, nitrogen, carbon dioxide gases were purchased from CV Retno Gas.

2.2. Pre-treatment of silica gel template

The silica gel 60 received as is from Merck was pretreated by heating at 200 °C for four hours [8]. The silica gel was used as a template in the hard templated mesoporous carbon synthesis. The purpose of the pre-treatment process is to remove water and other impurities from the silica gel.

2.3. Synthesis of soft templated mesoporous carbon

The soft templated mesoporous carbon (ST MC) synthesis adopted the procedure of Liang et al. [9] and Sulistianti et al. [10]. 1.25 g phloroglucinol and 1.25 g Pluronic F127 were dissolved in 9.7 g of 10:9 weight ratio of ethanol and water mixture and stirred at room temperature until the copolymer dissolution was completed. Then, 0.08 mL of 37 % (v/v) HCl was added to the solution and stirred until a light pink color appeared. Then, the addition of 1.25 mL of 37 % (v/v) formaldehyde was conducted to the synthesis solution, and stirred for 2 h until the mixture separated into two layers. The bottom layer was taken and stored while stirring overnight, then cured in an autoclave in an oven at 100 °C for 24 h [11]. Carbonization of the resulting monolith was performed in a tubular furnace with N2 gas flow using heating profile from 100 to 400 °C at the rate of 1 °C/min, from 400 to 850 °C at the rate of 5 °C/min, and finally samples were kept at 850 °C for 2 h under 10 cc/min nitrogen flow. The samples were later cooled down to room temperature under the same nitrogen environment [12]. The resulting carbons were then kept in desiccator.
2.4. Synthesis of hard templated mesoporous carbon
The synthesis of hard templated mesoporous carbon (HT MC) was conducted by following the recipe of Konwar et al. [8] with some modifications. The original procedure employed furfuryl alcohol as the carbon source and HF to remove the silica template, while this work used phloroglucinol carbon source and NaOH solution for desilication. In the typical procedure, 1.25 g phloroglucinol and 1.25 mL formaldehyde was added to 1.25 g pretreated dried silica gel. Then, stirring was performed on the mixture at room temperature for 72 h. Thereafter the silica gel filled with carbon precursors was filtered and dried at room temperature for 12 h. The pyrolysis of the material was carried out in a tubular furnace under nitrogen environment (100 ml/min) at 650 °C for 3 h. After pyrolysis, the silica gel–carbon composite was stirred in 1 M of NaOH solution at temperature of 90 °C for 10 min to remove the silica template. The desilication step was repeated two times followed with repeated washing with water:ethanol (1:1 w/w) mixture to ensure a complete removal of the template. The carbon was finally dried in an oven at 110 °C overnight.

2.5. Impregnation of Ni
A total of 0.45 g Ni(NO₃)₂·6H₂O was dispersed in 1 mL of water: ethanol solution with a comparative ratio of 1:1 (% w/w). Then, as much as 0.3 g of mesoporous carbon was added to the mixture. The mixture was then stirred for 6 h. The material was then reduced with H₂ gas flow at temperature of 600 °C for 6 h. This procedure allowed the Ni²⁺ reduction to Ni(0) [12]. The procedure was conducted for both soft and hard templated MC. The resulting materials denoted as ST Ni/MC and HT Ni/MC.

2.6. Carboxylation of phenylacetilene
In the catalysis application of each material (ST Ni/MC and HT/Ni MC), the reaction was carried out in the CO₂ atmospheric reactor. A total of 0.0312 g of catalyst, 0.052 g (0.8 mmol) Zn powder and 0.1624 g (0.8 mmol) MgCl₂·6H₂O were inserted into the reactor followed by 0.087 mL (0.8 mmol) phenylacetilene and 4 mL DMF. The flushing was carried out by flowing CO₂ gas for several minutes. Subsequently, a flow of 1 bar CO₂ was inserted into a balloon until it reached the maximum capacity. The reactor was then placed in an oil bath with the temperature of 85 °C and the CO₂ gas was then flowed. The mixture was stirred for various reaction times (2, 4, 6 and 8 h). The resulting products were then added by 1 mL of 10 % HCl solution, filtered and tested using HPLC.

2.7. Result characterization
The HPLC analysis of the resulted carboxylation product was conducted using C18 column (200 nm x 4.6 mm) with 5 μm particle size, UV-vis detector with the wavelength (λ) of 254 nm, eluent solution of methanol:1 % acetic acid with the ratio of 55:45 (v/v). Phenylacetic acid standard was measured in the concentration of 50, 100, 250, 500 and 1000 ppm. Meanwhile, phenyl propiolic acid standard was measured in the concentration of 5, 10, 25, 50, 100, 250, 500 and 1000 ppm. Samples with highest result were then co-injected with 250 ppm of phenyl propiolic acid to ensure that the compound measured at the retention time was indeed the desired product.

3. Results and discussion
3.1. Characterized by FTIR
Functional groups and absorption spectra were determined using FTIR as described in figure 1. The spectra of soft templated mesoporous carbon (ST MC) pre, post carbonization, and after impregnation are presented in figure 1a. On the spectrum of MC pre carbonization, there were several peaks attributed to the remaining phloroglucinol precursor and F-127 template at 3300 cm⁻¹ from stretching vibration of O-H, 2880 cm⁻¹ from stretching vibration of C-H, 1623 cm⁻¹ from bending vibration of O-H, 1468 cm⁻¹ bending vibration C-H and 1111 cm⁻¹ vibration of C-O. Those peaks were then disappeared after pyrolysis, indicating that the carbonization has conducted successfully. Meanwhile, FTIR spectra of
hard templated mesoporous carbon (HT MC) are presented in figure 1b. Vibration at 3500 cm\(^{-1}\) is attributed to O-H stretching, vibration at 1627 cm\(^{-1}\) is from O-H bending, and at 1456 cm\(^{-1}\) is attributed to C-H bending. There are also several peaks at 800, 950 and 1071 cm\(^{-1}\), which are respectively contributed to the vibration of Si-O, Si-OH and Si-O-Si formed in the framework of MC [13]. The peaks attributed to silica template were then decreased after desilication indicating that the stirring of HT MC into NaOH solution is effective to remove the remaining template.

3.2. Characterized by XRD

The crystallinity of synthesized material was determined using XRD. The XRD pattern of both templated MC before carbonization (figure 2) shows a single signal at 2\(\theta\) around 21°. After carbonization, the materials show 2\(\theta\) peaks around 23.67° (002) and 43.56° (100) revealing the presence of graphitic carbon [14]. Widened peak diffraction indicates the material has low crystallinity. This phenomenon can be caused by the collapse of some mesoporous carbon structures during
the carbonization process [15]. Meanwhile, the diffractograms of both material after impregnation show additional peaks at 44.5° (111); 51.8° (200) and 76.4° (220) which are attributed to Ni\(^0\) [13] and small peak at 62.8° for HT Ni/MC indicating there is a small amount of NiO.

### 3.3. Characterized by EDX

Based on EDX data for soft templated mesoporous carbon, the mean of C elemental measured by the instrument is 86.56 % (table 1). This number then decreases to 64.87 % after Ni impregnation allowing 25.79 % elemental Ni to be added to the percentage. The same phenomenon also happens on the hard templated mesoporous carbon, where the mean of C elemental is 81.86 % and decreased to 13.38 % after Ni impregnation. There is a small amount of the remaining Si template in hard templated mesoporous carbon even after desilication.

### 3.4. Characterized by SEM

The SEM image of Soft Templated MC and Hard Templated MC before and after impregnation with Ni are shown in figure 3. The morphology of soft templated MC is worm hole-like [11] with various pore diameter. The material after impregnation (ST Ni/MC) has a similar morphology with less visible pores. This phenomenon might be caused of Ni metal is being inserted into and/or spread on the surface of MC. Meanwhile, both hard templated MC before and after impregnation have more agglomeration on the surface. This may be attributed to the higher extent of sintering [8].

### 3.5. Characterized by BET

The surface area analysis showed that the ST MC has surface area of 24.079 m\(^2\)/g before the pyrolysis and of 431.807 m\(^2\)/g after pyrolysis. ST Ni/MC has the surface area of 292.944 m\(^2\)/g. The N\(_2\) adsorption/desorption isotherms obtained for ST MC (figure 4a) exhibits the typical type IV isotherm, with signature hysteresis loop revealing the presence of mesoporosity, as also revealed by the BJH pore size distribution (figure 5a). The average pore size of ST MC is 3.59 nm and of ST Ni/MC is 3.15 nm. The decrease of the average pore size might be caused of Ni spread on the surface of the mesoporous carbon. Based on the trend of hysteresis loop, it can be concluded that the pores have a cylindrical shape (type a). Meanwhile, HT MC has the surface area of 72.132 m\(^2\)/g and HT Ni/MC of 62.714 m\(^2\)/g. The lower surface area of HT MC compared to ST MC is due to the radius of beads silica template used in the synthesis of material. The average pore size of HT MC and HT Ni/MC is 1.93 nm and 1.94 nm. The adsorption isotherm and BJH pore distribution of HT MC are respectively presented in figure 4b and figure 5b.

### 3.6. Carboxylation

Phenyl propiolic acid is the main product of phenylacetylene carboxylation with CO\(_2\). The chromatogram of the carboxylation products is presented in figure 6a for ST Ni MC catalyst and figure 6b for HT Ni/MC catalyst with the retention time of around 4 min for phenyl propiolic acid. Peaks at 12 and 2 min retention time belong to the unreacted phenylacetylene and DMF, respectively. The phenyl propiolic acid showed best peaks at reaction time of 6 h for ST Ni MC catalyst with the area of 301 mAU and yield of 1.4 %. Meanwhile HT Ni/MC catalyst showed the best performance in phenyl propiolic acid formation at the reaction time of 8 h for with the area of 453 mAU and yield of 2.2 %.

### Table 1. Elemental composition of soft and hard templated carbon.

| No | Element | ST MC | ST Ni/MC | HT MC | HT Ni/MC |
|----|---------|-------|---------|-------|---------|
| 1  | C       | 86.56 | 64.87   | 81.86 | 13.38   |
| 2  | O       | 13.44 | 8.99    | 17.53 | 43.74   |
| 3  | Ni      | -     | 25.79   | -     | 42.87   |
| 4  | Si      | -     | -       | 0.60  | -       |
Figure 3. SEM image of (a) Soft Templated Mesoporous Carbon (ST MC), (b) Soft Templated Ni Mesoporous Carbon (ST Ni/MC), (c) Hard Templated Mesoporous Carbon (HT MC), and (d) Hard Templated Ni Mesoporous Carbon (HT Ni/MC).

Figure 4. Isotherm adsorption of (a) ST MC, and (b) HT MC.
Figure 5. Pore distribution of (a) ST MC and (b) HT MC.

Figure 6. Overlay chromatogram of carboxilation product with (a) ST Ni MC catalyst and (b) HT Ni MC catalyst.
4. Conclusion
Mesoporous carbon from phloroglucinol precursor has been synthesized using soft template and hard template method. The SEM analysis showed the ordered and uniform porous surface area of MC with the worm hole-like pore for ST MC and agglomerated surface morphology for HT MC. The BET analysis revealed that the ST MC and HT MC have surface area of 431 and 72 m²/g, respectively. XRD pattern of both MC showed peaks for 2θ around 23.67° and 43.56° which indicate the graphite crystallinity and additional peaks after Ni impregnation at 2θ of 44.5°, 51.8° and 76.4° which attributed to Ni²⁺. The Ni/MC catalyst has the potential of being utilized in carboxylation of phenylacetylene with carbon dioxide resulting phenyl propiolic acid with optimum reaction condition: temperature of 85 °C for 8 h contact time with the yield of 2.2 % for HT Ni/MC catalyst, and 6 h contact time with the yield of 1.4 % for ST Ni/MC catalyst.

Acknowledgments
This work is funded by International Indexed Publication for Student Research grant (PICTTA B) NoNKB-0635/UN2.R3.1/HKP.05.00/2019 from Directorate of Research and Community Engagement, Universitas Indonesia (DRPM UI) and assisted by Laboratory Directorate General of Customs and Excise (DGCE) in Jakarta.

References
[1] Juliá-Hernández F, Gaydou M, Serrano E, van Gemmeren M and Martin R 2016 Top. Curr. Chem. 374 45
[2] Supriadi A et al. 2016 Data Inventory Emisi GRK Sektor Energi (Jakarta: Pusat Data dan Teknologi Informasi Kementerian Energi dan Sumber Daya Mineral)
[3] Yu B, Diao Z-B, Guo C-X and He L-N 2013 Journal of CO₂ Utilization 1 60-8
[4] Pamungkas A Z, Abdullah I and Krisnandi Y K 2019 IOP. Conf. Ser. Mater. Sci. Eng. 496 012003
[5] Aziz M A A, Jalil A A, Triwahyono S, Muki R R, Taufiq-Yape Y H and Szegar M R 2014 Appl Catal B Environ. 147 359-68
[6] Ma T-Y, Liu L and Yuan Z-Y 2013 Chem. Soc. Rev. 2013 42 3977
[7] Pal N and Bhaumik A 2013 Adv. Colloid. Interfaces. Sci. 189-190 21-41
[8] Konwar R J and De M 2014 J. Anal. Appl. Pyrol. 107 224-32
[9] Liang C and Dai S 2006 J. Am. Chem. Soc.128 5316-17
[10] Sultistanti I, Krisnandy Y K and Munandar I 2017 IOP. Conf. Ser. Mater. Sci. Eng. 188 012041
[11] Gorka J, Zawislak A, Choma J and Jaroinec M. 2008 J Carbon 46 1159-61
[12] Chen C-S, Budi C S, Wu H-C, Saikia, D and Kao H-M 2017 ACS. Catal. 7 8367-81
[13] Zhang G, Liu J, Xu Y and Sun Y 2019 Int. J. Hydrogen. Energ. 44 4809-20
[14] Chiou J Y Z, Kung H-Y, Wang C-B 2017 J. Saudi. Chem. Soc. 21 205-09
[15] Liu R, Shi Y, Wan Y, Meng Y, Zhang F, Gu D, Chen Z, Tu B and Zhao D 2006 J. Am. Chem. Soc. 128 11652-62