Synthesis of impregnated nickel-mesoporous carbon and its application for reaction of acetylene with carbon dioxide

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Abstract. Mesoporous carbon has been synthesized using soft-template method with phloroglucinol as carbon precursor and pluronic F127 as a template to form mesosize pores in carbon structure. The Brunauer-Emmett-Teller (BET) results prove the existence of hysteresis loop and adsorption isotherm type IV with total surface area of 432.498 m²/g and pore diameter of 7.46 nm. The mesoporous carbon was then impregnated with various amount of nickel metal using Ni(NO₃)₂ as precursor, followed by four ways of reduction: (1) with ethylene glycol in aqueous solution; (2) with ethylene glycol in 98% ethanol in water; (3) with NaBH₄; and (4) with H gas. Energy Dispersive X-Ray (EDX) analysis shows that nickel content in materials after reduction were (1) 34.48 %, (2) 0.02 %, (3) 0.9 % and (4) 1.73 %, in respective to the reduction methods. X-Ray Diffraction (XRD) patterns of mesoporous carbon reduced with NaBH₄ and H, show no change in mesoporous carbon structure, especially for peak at 20 of 24.44° and 43.18°. After impregnation, the materials were further tested for their catalytic activity for acetylene reactions with CO. The reactions were conducted in a 100 mL batch reactor with a pressure ratio of acetylene to CO of 0.2:0.8. Some reaction conditions were examined to determine the effect on the reaction: reaction time (3, 6, 12) h and reaction temperature (25, 40 and 80) °C. Product analysis using High Performance Liquid Chromatography (HPLC) shows that new peak appears at retention time of 3.625 minutes. The optimum condition was obtained at 25 °C and 3 hours.

Keywords: nickel catalyst, mesoporous carbon, acetylene, CO utilization

1. Introduction

Carbon dioxide is one of the greenhouse gases that keep the earth's surface to remain warm. However, when its concentration increase excessively, the surface temperature of the earth may increase, causing climate change. Therefore, it is important to reduce CO₂ concentration in the atmosphere to minimize its negative effect to global community. There are two technologies for reducing CO₂ concentration, Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) [1]. CCU in addition to CO₂ capture also converts CO₂. The suspended CO₂ is more active than the gas phase so conversion is more efficient [2]. CCU technology is able to convert CO₂ into a more valuable chemical [3-4]. Various catalysts have been developed to assist the process associated with the transformation of CO₂ to liquid or solid products. Various types of catalysts used were homogeneous catalysts, which, although efficient in chemical reaction, were difficult to be separated from the reaction system. Therefore, solid support is needed to heterogenize those homogeneous catalysts. One of the materials used as catalyst support is mesoporous carbon, which has a large surface area, large pore volume and specific physical surface properties. In 2015, Yu et al. [5] reported the use of activated carbon as copper support for carboxylation of terminal...
alkynes [8]. Although the solid catalyst shows high activity but the product was alkyl 2-alkynoate, not alkyl prop-2-enoic acid, the product of Ni-catalyze hydrocarboxylation. Similar result was obtained when using AlO as copper support for the same reaction [9]. However, no studies have examined the potential of nickel catalysts impregnated on mesoporous carbon as the catalyst for CO reactions with acetylene.

2. Experimental

2.1. Synthesis of mesoporous carbon (MC)

Synthesis of mesoporous carbon was carried out using previously reported procedure [10–11]. In a typical synthesis, 1.25 g of phosphogluconol and 1.25 g of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (Pluronic F127) were dissolved into 9.7 g of 10:9 weight ratio of ethanol and water mixture. After the solid dissolved completely, 0.08 ml of 37 % HCl was added to the solution and stirred for 30 min until a light pink color appeared. The solution was then added by 1.25 ml of 37 % formaldehyde. After 30 min, the solution turned cloudy and separated into two layers after 1–2 h. The polymer-rich bottom layer was taken and continued stirring overnight to form elastic, non-sticky monolith. The obtained monolith was then transferred to an autoclave and cured in oven at 100 °C for 24 h. The material was carbonized in tubular furnace under nitrogen flow with heating rate of 1 °C/min from 100 to 400 °C and 5 °C/min from 400 to 850 °C and finally kept at 850 °C for 2 h.

2.2. Impregnation of nickel

The impregnation of nickel was conducted by two methods: dry impregnation (incipient-wetness) and wet impregnation. For wet impregnation, the method was adopted from our previous reported procedure [12]. In a typical procedure, 0.5 g of mesoporous carbon was introduced into a glass cup containing 10 mL of water. A total of 1.23 g Ni(NO₃)₂·6H₂O which has been dissolved in 5 mL water was added dropwise. The mixture was then stirred for 6 hours, and the product was filtered. For dry impregnation, 1 g of mesoporous carbon was introduced into a glass cup, then 1.70 mL of Ni(NO₃)₂ solution (prepared by dissolving 0.6262 g Ni(NO₃)₂·6H₂O in 10 mL water) was added dropwise and stirred for 24 hours.

2.2.1. Reduction with ethylene glycol (water solvent). The mixture from 2.2 (wet impregnation) was placed into a round-bottom flask containing 20 mL of ethylene glycol and heated by reflux at 170 °C for 6 hours. The resulting solid was then filtered and dried.

2.2.2. Reduction with ethylene glycol (water-ethanol solvent). The mixture from 2.2 (wet impregnation) was placed into a round flask containing 20 mL of ethylene glycol and heated by reflux at 170 °C for 6 hours. The resulting solid was then filtered, washed with water-ethanol and dried.

2.2.3. Reduction with NaBH₄. A total of 0.2605 g NaBH₄ was dissolved in 50 mL of water. Then the Ni-impregnated mesoporous carbon (dry impregnation) was stirred with 5 mL of NaBH₄ solution for 30 minutes. Then, the mixture was poured into a quartz tube and dried under H₂ flow with a temperature of 550 °C for 6 hours.

2.2.4. Reduction with H₂. The Ni-impregnated mesoporous carbon (dry impregnation) was poured into a quartz tube and dried under H₂ flow with a temperature of 550 °C for 6 hours.

2.3. Catalysis test

The carboxylation reactions were carried out by using a 100 mL round bottom flask as reactor equipped with thermometer and gas balloon. To the glass reactor, 0.05 g catalyst, 0.032 g promoter (MgCl₂), 0.011 g Zn powder, 0.15 mL H₂O, and 10 mL DMF were introduced. CO₂ and acetylene gas with mol ratio of 4:1 were then dialed with a flow rate of 100 mL/min for 1.5 minute. Variation of reaction time (3, 6 and 12) h and temperature (25, 40 and 80) °C were examined to see their effect on reaction.

3. Results and discussion

In figure 1, the material before carbonization (non MC; spectrum number 1) shows an OH stretching peak indicated by a widening peak at about 3500 cm⁻¹ originating from phosphogluconol group. There is
Table 1. Comparison of EDX characterization results

| Elements (% mass) | Ni@MC reduction methods |  |  |  |
|------------------|-------------------------|---|---|---|
|                  | ethylene glycol (water) | ethylene glycol (water:ethanol) | NaBH | Ni@MC reduced with H. |
| C                | 35.31                   | 90.15                      | 91.45 | 89.01 |
| O                | 30.20                   | 9.83                       | 7.573 | 9.26  |
| Ni               | 34.48                   | 0.02                       | 0.9   | 1.73  |

Figure 1. FTIR spectra of (1) Ni non MC, Ni@MC reduced with (2) ethylene glycol (water), (3) ethylene glycol (water:ethanol), (4) H, (5) NaBH₄, and (6) Ni@MC after carbonization

Figure 2. SEM Images with magnification of 300 times for Ni@MC reduced with (a) ethylene glycol (water solvent), (b) ethylene glycol (water:ethanol solvent), (c) NaBH₄, and (d) H, gas.

also a methylene group indicated by a peak at a wavelength of 2900 cm⁻¹ derived from a bond between formaldehyde and phloroglucinol. The Fourier Transform Infrared (FTIR) spectrum after carbonization (spectrum number 6) shows the loss of the methylene vibration peak, while the peak of the OH stretching still appears but with low absorption intensity. This indicates that the carbonization process has proceeded well. FTIR spectra of the materials after Ni impregnation and reduction are shown in figure 1 spectrum number 2 to 5. Based on the figure, it can be seen that reduction with ethylene glycol still leaves the -OH group in the material as indicated by the appearance of a widening peak at a wavenumber of around 3500 cm⁻¹. Whereas, the reduction with NaBH₄ and H reduce or even eliminate the -OH group from the material as indicated by peak loss from the -OH group vibration.

Figure 2 shows the morphological image of the four types of catalysts. Figure 2a shows MC@Ni reduced with ethylene glycol (water), figure 2b shows MC@Ni reduced with ethylene glycol (ethanol:water), figure 2c shows MC@Ni reduced with NaBH₄, and figure 2d shows MC@Ni reduced with H. These four images show the surface of the impregnated nickel metal on mesoporous carbon.

Table 1 shows the elemental composition of the materials obtained by four different reduction methods from Energy Dispersive X-Ray (EDX) analysis. Reduction using ethylene glycol with water
Figure 3. XRD pattern of (a) mesoporous carbon and (b) Ni@MC that reduced with (1) ethyleneglycol (water), (2) ethyleneglycol (water:ethanol), (3) NaBH$_4$ and (4) H$_2$.

Figure 4. Typical HPLC chromatogram of the reaction mixture (obtained for the reaction conducted at 25 °C for 3 hours)

solvent gave the highest Ni content of 34.48 % while the reduction using ethylene glycol with water:ethanol solvent gave the smallest Ni content of 0.02 %. The big difference in Ni content of the two methods occurs because in the second method, the material that has been produced was then washed again with ethanol-water solvent, which causes the leaching of impregnated Ni species. Similar result is occurred for reduction with NaBH$_4$ and with H$_2$ gas. The reduction result using NaBH$_4$ gave a smaller Ni content than the reduction using H$_2$ gas. This happens because in reduction with NaBH$_4$, Ni@MC was stirred in NaBH$_4$ solution for 30 minutes, which allows Ni leaching to occur during the process. Whereas in the reduction method with H$_2$, there was no addition of solvent, and the reduction process was done by flowing H$_2$ gas at high temperatures.

X-Ray Diffraction (XRD) characterization aims to determine whether the impregnation of Ni metal on mesoporous carbon changes the structure and crystallinity of the support. Figure 3a shows the typical peak of mesoporous carbon at 20 of 24.44° and 43.18°, which related to (002) and (101) plane [11]. Based on XRD diffraction pattern analysis, there is no peak other than the typical peak of mesoporous carbon. The crystallinity of the mesoporous carbon is indicated by a widened peak, where the crystal is amorphous. This shows that the addition of nickel did not alter the structure of the mesoporous carbon. Based on the XRD diffraction pattern, there is no peak for Ni. This can happen because the % Ni contained in the material is too small to be detected by XRD. In the XRD pattern for the reduction results using ethylene glycol (water), new peaks emerge at 34 ° and 60 ° as indicated by star symbol. Those two emerging peaks indicate the presence of Ni(II)and Ni(0) species [12].

Next, Ni@MC with Ni content of 34.48 % was used as catalyst in the reaction between acetylene and CO$_2$ at ambient pressure. At first, it was expected that acrylic acid would be the product of the reaction. However, analysis of the reaction mixture with High Performance Liquid Chromatography (HPLC) showed no peak, which indicated the presence of acrylic acid (6.9 minutes of retention time). Instead, new peaks appear at a retention time of around 3.6 minutes as shown in figure 4. The new peak shows the possibility of new compounds formed. Previously these peaks did not appear on the blank solution (obtained from the reaction conducted in the absence of catalyst).
Table 2. Comparison of the peak area of new products in various reaction conditions

| Reaction time (h) | Reaction temperature (°C) |
|------------------|---------------------------|
|                  | 25       | 40       | 80       |
| 3                | 40.6316  | 34.9610  | 27.9699  |
| 6                | 38.8019  | 21.4017  | 23.1116  |
| 12               | 42.2104  | 29.8603  | 27.7182  |

Complete data from the catalysis reaction between acetylene and CO2 are presented in table 2. The formation of the product seems to be preferred to occur at low temperatures (25 °C). While the time variation does not significantly influence the number of products formed. Generally in the catalytic reaction, the higher the temperature, the more effective the reaction will be. However, at low temperature the gases tend to be easily dissolved in the solvent (DMF), making it possible to come into contact with catalysts and promoter, thus causing more reaction to occur. When the reaction is carried out at high temperatures, there will be a competition between temperatures to lower the activation energy to the temperature that will complicate acetylene to interact with carbon dioxide.

4. Conclusions
Mesoporous carbon impregnated nickel has been successfully synthesized without damaging the carbon structure. Mesoporous carbon impregnated nickel has a catalytic ability for the reaction between acetylene with carbon dioxide. Further investigation needs to be conducted to determine the product.

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References
[1] Songolzadeh M, Ravanchi M T and Soleimani M 2012 International Scholarly and Scientific Research & Innovation 6(10) 900–7
[2] Saha D and Deng S 2010 J. Colloid Interface Sci. 345 402–9
[3] Liu Y, Wang Z U and Zhou H C 2012 Greenhouse Gas Sci. Technol. 2 239–59
[4] Li Y N, He L N, Liu A H, Lang X D, Yang Z Z, Yu B and Luan C R 2013 Green Chem. 15 2825–9
[5] Liu A H, Yu B and He L N 2014 Greenhouse Gas Sci. Technol. 5 17–33
[6] Lejkowski M L et al. 2012 Chem Eur. J. 18 14017–25
[7] Vavasori A, Calgaro L, Pietrobon L and Ronchin L 2018 Pure Appl. Chem. 90 315–26
[8] Yu B, Xie J N, Zhong C L, Li W and He L N 2015 ACS Catal. 5 3940–4
[9] Bondarenko G N, Dvurechenskaya E G, Magommedov E S and Beletskaya I P 2017 Catal. Lett. 147 2570–80
[10] Górka I, Zawisłak A, Choma J and Jaroniec M 2008 Carbon 46 1159–74
[11] Wang Y, Bai X, Wang F, Qin H, Yin C, Kang S, Li X, Zuo Y and Cui L 2016 Sci. Rep. 6 26673
[12] Yung T Y, Huang L Y, Chan T Y, Wang K S, Liu T Y, Chen P T, Chao C Y and Liu L K 2014 Nanoscale Res. Lett. 9 444