Preliminary study on carboxylation reaction of phenylacetylene with CO₂ using nickel catalyst impregnated on mesoporous carbon

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Abstract. In this research, carboxylation reaction of phenylacetylene with CO₂ has been studied using impregnated nickel on mesoporous carbon as catalyst. Mesoporous carbon was successfully synthesized using a soft template method with Pluronic F127 as pore template, and formaldehyde and phloroglucinol as the carbon source. This material was characterized with Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Brunauer-Emmett-Teller (BET) analysis. Characterization with XRD shows the presence of two peaks at 24.26° and 42.76° which denotes the typical peak of graphite-like carbon. BET surface area analysis shows that the mesoporous carbon has a pore size distribution of 7.2 nm and surface area of 432.15 m²/g. Modification of mesoporous carbon was carried out by impregnation of Ni metal into mesoporous carbon (Ni@MC) through reduction of Ni(II) with ethylene glycol. The Ni@MC catalyst was used as a catalyst in the carboxylation reaction of phenylacetylene with CO₂. The reactions were carried out in a batch reactor under various reaction conditions. High Performance Liquid Chromatography (HPLC) analysis of the product mixtures revealed that the highest yield of trans-cinnamic acid (2.83 %) was achieved at 85 °C for 12 h reaction time.

Keywords: mesoporous carbon, nickel, carboxylation, phenylacetylene

1. Introduction

CO₂ gas is one of the compounds that its existence in nature is very abundant. CO₂ is an inert, non-toxic, non-flammable, and the largest contributor to greenhouse gases causing the earth’s surface temperature to rise. Rising earth surface temperatures is noted as Global Warming. Global Warming is a phenomenon of the earth’s escalating temperature due to the increase of greenhouse gases such as CO₂, CH₄, N₂O, and CFCs, so that solar energy is trapped in the earth's atmosphere and cannot be released out of the atmosphere.

One way to reduce CO₂ emissions is by utilizing Carbon Capture and Storage (CCS) and Carbon Capture Utilization and Storage (CCUS) technologies. CCS is a technology used to reduce the increase in greenhouse gas emissions sourced from CO₂ gas. In the CCS technique, CO₂ is captured and then separated and stored. This technique is commonly applied at mining areas that produce a lot of CO₂ gas, usually used in Enhanced Oil Recovery (EOR) by injecting CO₂ into the bowels of the earth to push the oils left inside to get out. Whereas in CCUS technique, CO₂ can be reacted with another reagent to produce a product that has economic value, one of which is acrylic acid and its derivatives, which are needed in various industries as intermediate compounds in the production process. For example, Na acrylate is very important in the industry, commonly used as a monomer in a polymer super-absorber and its sales can reach 4 million tons globally [1]. Conversion of CO₂ provides many advantages, in addition to reducing CO₂ emission; it can also produce high-value products [2]. However, due to its inert character, CO₂ is difficult to react with other compounds, so a catalyst is required. One of the most commonly used catalysts in CO₂ activation is nickel [3]. Nickel is included
in inexpensive metals and is usually used in the form of its complex compounds, so the catalysis system is homogeneous. There are some examples of utilization of homogeneous nickel catalyst in carboxylation reaction of some unsaturated compounds such as alkynes [4] and ynamides [5]. Thus, immobilization of the nickel homogeneous catalyst, by attaching it to a solid support, could provide various advantages provided by heterogeneous catalyst, especially for industrial scale applications, such as ease of separation, thermal and another durability.

There are some reports on the use of heterogeneous metal catalyst on carboxylation reaction of unsaturated hydrocarbons with CO. The carboxylation reaction of the terminal alkynes with CO, has been successfully performed by using Cu nanoparticle catalyst with AlO support to produce alkynyl carboxylic acid derivatives (R-COOtBu) but it requires a high pressure [6]. Furthermore, the carboxylation reaction of the terminal alkyne with CO/H, has also been successfully carried out using dual catalyst NHC-Ag/Pd to produce R-COOH compounds [7]. However, it is well known that Pd catalyst is expensive. Activated carbon has also been reported as catalyst support for some metals such as copper [8] and silver [9] to produce alkynyl carboxylic acids and carbonates, respectively. However, the product was different from the Ni-catalyzed carboxylation product.

In this work, the carboxylation reaction of terminal alkyne was conducted using impregnated Ni catalyst on mesoporous carbon as heterogeneous catalyst. To the best of our knowledge, this kind of work has not been reported. The carboxylation reaction was carried out at atmospheric pressure and low temperature, using phenylacetylene as the alkyne, and as results, similar compound to cinnamic acid was obtained as the product.

2. Experimental

2.1. Materials

All chemicals used in this experiment were analytical grade and used without further purification. Phloroglucinol, Pluronic F127, Ni(NO3)6H2O, MgCl2, zinc powder, formaldehyde, DMF 99.8 %, phenylacetylene 98 %, and trans-cinnamic acid 97 % were purchased from Sigma Aldrich. Ultra-high purity CO gas was purchased from CV Retno Gas.

2.2. Synthesis of mesoporous carbon (MC)

Synthesis of mesoporous carbon was carried out using a previously reported procedure [10]. In a typical synthesis, dissolution of 1.25 g of phloroglucinol and 1.25 g of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (Pluronic F127) was conducted in the mixture of 9.7 g of 10:9 weight ratio of ethanol and water. After the solid completely dissolved, 0.08 mL of 37 % HCl was inserted into the solution and stirred for 30 min until a light pink color is observed. The solution was then added with 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 (12 h) to form an elastic, non-sticky monolith. The obtained monolith was then displaced into an autoclave and cured in an oven at 100 °C for 24 h. The material was carbonized in a tubular furnace under nitrogen flow with the heat rate of 1 °C/min from 100 to 400 °C and 5 °C/min from 400 to 850 °C and finally maintained at 850 °C for 2 h.

2.3. Impregnation of Ni into mesoporous carbon (Ni@MC)

Impregnation of Ni into mesoporous carbon was conducted using previously reported method [11]. 0.5 g of MC was dispersed into 10 mL of water. 1.23 g of Ni(NO3)6H2O was dissolved into 5 mL of water and then added drop wise into the dispersed carbon. The mixture was stirred for 6 h and dried in air. The obtained material and 20 mL of ethylene glycol were transferred into a round-bottom flask and the compound was heated under reflux at 170 °C for 6 h. The final solid was filtered, washed by water and ethanol, and dried at room temperature.

2.4. Carboxylation reaction

Phenylacetylene (0.8 mmol), Ni@MC (0.04 mmol), MgCl2 (0.6 mmol), Zn (0.6 mmol) and DMF (4 mL) were mixed in the reactor at room temperature. Then, balloon filled with CO gas was fitted to the reactor. The air in the reactor was removed by flowing the CO gas into the reactor and then closed. The mixture was stirred for 12 h at 50 °C and 1 atm. The time and temperature of reaction were varied: (8 h, 12 h and 16 h) and (25 °C, 50 °C, 85 °C). To obtain the targeted product i.e. cinnamic acid, the mixture was multi-extracted with CHCl3 (3 x 5 mL). The organic layer was collected, and the
aqueous layer was acidified with 10% HCl (2 mL), then extracted with diethyl ether (3 x 5 mL). A collection of organic layers was taken and then dried with sodium sulfate (Na₂SO₄) then decanted. The remaining solvent was evaporated to obtain a dry white powder (cinnamic acid). The product was then analyzed and identified using HPLC. The product analysis was performed using the Diamonsil C18 column (200 mm x 4.6 mm, 5 μm particle size). The detector used was UV-Vis, which operated at the wavelength (λ) of 278 nm. The mobile phase used was methanol and 1% acetic acid with a ratio of 55:45 (v/v). The flow rate of the mobile phase was 1 mL/min. All analysis was performed under isothermal conditions at 25 °C [12].

3. Results and discussion
Morphology of MC and Ni@MC were examined with scanning electron microscope (SEM) and the results are shown in figure 1. All materials seem to have rough surface with various sizes. Ni@MC has a coarser morphology when compared to mesoporous carbon morphology (MC). This may be due to the presence of NiO and Ni(0) attached to the mesoporous carbon thus altering the surface. This surface characteristic might increase the surface area of Ni@MC, which could be useful for catalysis application.

From figure 2, it is shown that Ni particles were evenly distributed although there are some spots that do not contain Ni. The images also indicate that nickel species existed on mesoporous carbon
Figure 3. XRD patterns of (a) MC and (b) Ni@MC

Figure 4. FTIR spectrum of (a) MC and (b) Ni@MC

were mixture of both Ni(0) and NiOx, since oxygen atoms appeared at almost the same location to that of nickel, figure 2d. The presence of Ni(0) metal is shown as blue area in overlay image. The existence of this zero valent nickel is important since it could be the active catalyst site for carboxylation reaction. The existence of NiO in the materials could be explained by two reasons: it might be due to incomplete reduction during reflux with ethylene glycol, or there were some Ni(0) being re-oxidized by air during material characterization.

The diffraction pattern of MC and Ni@MC are shown in figure 3. In XRD pattern of both materials, there are two peaks at around 24° and 43° which shows the typical peak of lattice planes (002) and (101), respectively, in carbon material. This is in agreement with JCPDS File Index for carbon-based materials, No. 75-1621f.

In the diffraction pattern of Ni@MC, there are new peaks located at 34.04° (111) indicated by the star symbol and at 60.33° (012) indicated by the triangle symbol. These peaks are the peak of NiO (111) and Ni (012), according to the Ni-NiO diffraction pattern reported by Yung et al. [14].

Figure 4 shows that the FTIR spectra of Ni@MC look almost identical to that of MC. The absence of C-H stretching peak at 2900-3000 cm⁻¹ indicates no organic compounds remain in the materials. However, there are some new peaks in Ni@MC FTIR spectra at 1600 and 1100 cm⁻¹. This could be due to the presence of Ni-NiO species impregnated into mesoporous carbon.
Table 1. Results of carboxylation reaction.

| Entry | Reaction conditions | Yield of trans-cinnamic acid (%) |
|-------|---------------------|----------------------------------|
| 1     | 25 °C, 8 h          | Not detected                     |
| 2     | 25 °C, 12 h         | Not detected                     |
| 3     | 25 °C, 16 h         | Not detected                     |
| 4     | 50 °C, 8 h          | Not detected                     |
| 5     | 50 °C, 12 h         | Not detected                     |
| 6     | 50 °C, 16 h         | Not detected                     |
| 7     | 85 °C, 8 h          | 1.52                             |
| 8     | 85 °C, 12 h         | 2.83                             |
| 9     | 85 °C, 16 h         | 0.62                             |

Figure 5. BET N$_2$-surface area analysis: (a) Adsorption desorption isotherm and (b) BJH desorption MC.

The N$_2$ adsorption-desorption isotherm curve of mesoporous carbon is shown in figure 5. In the N$_2$ desorption adsorption process, a hysteresis loop is generated which can indicate the type of isotherm curve. The resulting MC isotherm curve indicates an IV type isotherm curve corresponding to the IUPAC type of adsorption curve. This type of isotherm curve is also supported by the distribution of pore size diameter. From the mesoporous carbon desorption BJH curve, it is shown that the pore size diameter is concentrated at 7.2 nm. Thus, the pore size diameter is in the range of mesoporous pore size (2–50 nm).

The results of the carboxylation reaction of phenylacetylene with CO$_2$ are shown in table 1. Based on HPLC analysis of reaction mixtures, trans-cinnamic acid (C$_6$H$_5$CH=CHCOOH) was detected as product when the reactions were conducted at 85 °C (entries 7-9). Conducting the reactions at lower temperatures gave no desired product (entries 1–6). The reaction of carboxylation of phenylacetylene with CO gave highest yield at 85 °C for over 12 h (entry 8). These results indicate that high temperature is required for carboxylation of phenylacetylene using heterogeneous Ni catalyst.

4. Conclusions
Modification of mesoporous carbon has been conducted by impregnation of Ni metal into mesoporous carbon (Ni@MC). The Ni@MC catalyst was used as a catalyst in the carboxylation reaction of phenylacetylene with CO$_2$. The highest yield of cinnamic acid (2.83 %) was achieved at 85 °C for 12 h reaction time.
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