Synthesis of impregnated Ni(0) zeolite ZSM-5 as catalyst for carboxylation reaction of acetylene with CO.

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Abstract. Conversion of carbon dioxide (CO$_2$) into other compounds has become very advantageous because of the abundance in the atmosphere. However, carbon dioxide (CO$_2$) is thermodynamically and kinetically stable so it needs low valence metal such as Ni(0) to be activated and react with other compounds. In this study, nickel metal-impregnated ZSM-5 was prepared as heterogeneous catalyst for carboxylation reaction of acetylene with carbon dioxide. Microporous and hierarchical ZSM-5 were synthesized using single template and double template, respectively. X-Ray Diffraction (XRD) characterization results show that ZSM-5 material with high crystallinity was successfully synthesized. Scanning Electron Microscopy (SEM) images show ZSM-5 has hexagonal coffin-like morphology. Brunauer-Emmett-Teller (BET) surface area analysis proves that the ZSM-5 has combination of micro and meso-sized pores (hierarchical pores). The elemental analysis using Atomic Absorption Spectroscopy (AAS) gives nickel content of 1.9 % in microporous ZSM-5 and 2.1 % in hierarchical ZSM-5. HPLC analysis show new peak is observed at retention time of 3.6 minutes for carboxylation reaction of acetylene (CO$_2$: acetylene of 0.2:0.8) with optimum condition at 12 h and 80 °C when using microporous Ni/ZSM-5 or hierarchical counterpart as catalyst.

Keywords: carboxylation, microporous Ni(0)/ZSM-5, hierarchical Ni(0)/ZSM-5, acetylene, CO$_2$ transformation

1. Introduction
Global warming is a problem that arises mainly due to excess of greenhouse gases (e.g. carbon dioxide, methane, nitrogen oxide) in the atmosphere, covering the earth and reflecting heat radiation back to the surface of the earth. This leads to problems in the environment such as rising sea level due to polar ice melting, increasing atmospheric storms, increasing species and organisms that cause disease [1]. In recent years, emissions from carbon dioxide gases generated by human activities such as industrial have become very high [2]. Accumulation of carbon dioxide in the atmosphere has huge risk because carbon dioxide can last longer than other greenhouse gases in the atmosphere. Therefore, some methods are required to reduce the accumulation of carbon dioxide in the atmosphere, such as CO$_2$ storage and utilization of CO$_2$ [3].

Conversion of carbon dioxide into other compounds becomes very advantageous yet challenging. Because carbon dioxide has a thermodynamic and kinetic stability so it needs low valence metal to react [4]. Currently there has been several carbon dioxide conversion using metal complexes catalyst [5]. However, most of the catalysts are homogeneous catalysts which are efficient in reaction but difficult to be separated from the products. For example, homogeneous nickel catalyst has been employed as good catalyst in carboxylation of various unsaturated hydrocarbons such as cyanamides for production of amino acid derivatives [6], and ethylene for production of acrylic acid [7]. ZSM-5 has been used widely as catalysts and catalyst support in many reactions. For example, Co/ZSM-5 as...
catalyst in partial oxidation of methane to methanol [8,9], conversion of biomass to levulinic acid [10], cracking of hexadecane [11], and conversion of CO to cyclic carbonates [12]. ZSM-5 modified with nickel is considered as an efficient heterogeneous catalyst for carboxylation reaction [13] because ZSM-5 has large pore size and high surface area makes it possible to be used as catalyst system that can convert carbon dioxide that is absorbed efficiently.

This work reports carboxylation reaction of acetylene with carbon dioxide, using nickel impregnated ZSM-5 zeolite. Hierarchical ZSM-5, synthesized using double template method, was used and its activity was compared with that from micoporous ZSM-5.

2. Experimental

2.1. Materials
The materials used were tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich), sodium aluminate (Sigma Aldrich), tetra propylammonium hydroxide (TPAOH, 1M, Sigma Aldrich), poly(diallyldimethylammonium chloride) (PDDAM, 35%, Aldrich), nickel(II) nitrate (Ni(NO)₂·6H₂O, Sigma Aldrich), ethylene gas (99.99 % UHP from BOC), N₂ gas (99.99 % UHP), H₂ gas (99.99 % UHP), CO₂ gas (99.99 % UHP), magnesium chloride (MgCl₂, Merck), dimethylformamide (DMF, merck), and deionized water. All materials in this work were used without further purification.

2.2. ZSM-5 synthesis and Ni/ZSM-5 preparation
The synthesis method is similar to that reported by Wang et al. [14] with some modifications [8]. Hierarchical ZSM-5 was synthesized using a molar ratio of 1 Al₂O₃ : 64 SiO₂ : 10 (TPA)₂O : 3571 H₂O. The water contained in the obtained zeolite was removed by drying at room temperature and then calcined at 823 K. Metal insertion into the zeolite was carried out using a wet impregnation method with reduction via hydrogen gas; 1 g of ZSM-5 was added to 0.2495 M nickel nitrate hydrate and stirred for 24 h at room temperature and was calcined at 823 K under flowing hydrogen gas. The ZSM-5 and Ni/ZSM-5 zeolites were characterized with X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) Shimadzu Prestige 21, Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDX) SEM FEI quanta FEG 450, and Atomic Absorption Spectroscopy (AAS) Shimadzu AA 13000.

2.3. Catalytic test: carboxylation of acetylene
Into a 100 mL round bottom flask reactor, 0.05 g Ni/ZSM-5 catalyst, 0.032 g promoter MgCl₂, 0.011 g Zn, 0.15 mL H₂O and 10 mL DMF were added. Then, flowed gas acetylene with a pressure of 0.2 atm and gas CO₂ with a pressure of 0.8 atm for 90 sec of each gas. The reactor was heated with temperature variation of (298, 313, 353) K with time variation of (3, 6, 12) h. After the reaction was completed, the autoclave was cooled to room temperature and the resulting product was collected for analysis with High Performance Liquid Chromatography (HPLC) Ultimate 3000, in which the column used was C18 3.5 μm, 4.6 x 150 mm, temperature 313 K, UV spectrum 210 nm and eluents used were acetonitril and 0.1 % HPO₄.

3. Results and discussion

3.1. Characterization of ZSM-5
Microporous ZSM-5 was prepared with single template tetrapropylammonium hydroxide (TPAOH) as mordenite inverted framework (MFI) structure directing agent while hierarchical ZSM-5 was produced with double template TPAOH and PDDAM as mesoporous structure template using hydrothermal method. During aging, the positive charge of PDDAM interacts with the negative charge of ZSM-5 crystal to be structured, so the ZSM-5 MFI framework could be grown around the PDDAM polication [14]. The XRD pattern of as-synthesized both microporous and hierarchical ZSM-5 (figure 1a) shows certain peaks in the 2θ range from 7° to 9° and from 22° to 25°, which is consistent with the standard ZSM-5 pattern [14], indicating that the ZSM-5 structure was successfully synthesized. Figure 1b shows the XRD patterns of modified ZSM-5 catalysts. From both microporous and hierarchical ZSM-5, some peaks were identified at position 20 about 44.5° and 53° indicating the presence of nickel(0) species [15].

Figure 2 presents the FTIR spectra of microporous and hierarchical ZSM-5 before (a) and after (b) calcination. The spectrum of both ZSM-5 before calcination shows several extra peaks at 2960–
Figure 1. XRD patterns of (a) microporous and (b) hierarchical ZSM-5 for as-synthesized ZSM-5 (red lines) and Nickel/ZSM-5 (brown and black lines).

Figure 2. FTIR spectra of (a) microporous and (b) hierarchical ZSM-5 zeolites before (black lines) and after (red and blue lines) calcination at 823 K.

Figure 3. SEM image of hierarchical ZSM-5, 30000 magnification.
Table 1. Results of acetylene carboxylation using Ni(0)/ZSM-5 (area below the peak of the product)

| Reaction temperature (K) | Ni/ZSM-5 (hierarchical) | Ni/ZSM-5 (microporous) |
|--------------------------|--------------------------|------------------------|
|                          | 3h | 6h | 12h | 3h | 6h | 12h |
| 298                      | 34.9968 | 36.8503 | 42.0126 | 0.1430 | 32.2852 | 29.0601 |
| 313                      | 27.7825 | 27.7568 | 41.6828 | 42.8235 | 34.2039 | 46.9155 |
| 353                      | 40.4486 | 21.7988 | 61.3878 | 10.6264 | 27.2937 | 49.6533 |

Figure 4. Chromatograph of product from carboxylation reaction of acetylene on hierarchical Ni(0)/ZSM-5 (condition: CO₂: acetylene: 0.2 : 0.8, 298 K, 12 h, catalyst 50 mg)

2850 cm⁻¹ (C–H stretching) and at 1470–1350 cm⁻¹ (C–H bending) compared with both ZSM-5 after calcination. These peaks show the presence of templates used in the synthesis of zeolite (TPAOH and PDDAM). Calcination was used to remove the templates used in the synthesis of both microporous and hierarchical zeolites. From figure 2b it can be seen that the extra peaks are gone and indicated the template were fully removed.

Figure 3 shows the SEM image of hierarchical ZSM-5. It can be seen that the ZSM-5 crystals have hexagonal shape and high crystallinity. Calculated from EDX data, the Si/Al ratio was 27.

Ni/ZSM-5 heterogeneous catalysts were synthesized using a wet impregnation method. The elemental analysis using AAS indicates that the loading of nickel on hierarchical ZSM-5 zeolites was about 2.1 wt.% and microporous ZSM-5 was 1.9 wt.%. This is close to the target loading of 2.0 wt.%.

3.2. Carboxylation of acetylene

Figure 4 shows a typical chromatograph of products from carboxylation reaction of acetylene on hierarchical Ni(0)/ZSM-5. It can be seen that there is a new peak with retention time (Rt) of 3.647 min, after reaction took place at 353 K and 12 h, while using hierarchical or microporous Ni(0)/ZSM-5 catalyst. This new peak should be more polar than the expected acrylic acid (a published Rt for acrylic is 6.9 min [16]), when using C18 column with acetonitrile and phosphoric acid (0.1 % H₃PO₄) as eluent. While table 1 summarizes the results obtained in various reaction conditions, where the optimum condition took place at 353 K and 12 h.

Figure 5 is the FTIR spectra of the reaction products. A broad band assigned to vibration of O-H appeared at 3600–3400 cm⁻¹, while sharp peaks attributed to vibration of C-H at 2950–2840 cm⁻¹, vibration of C=O at 1680 cm⁻¹, bending vibration of –C=H at 1480–1440 cm⁻¹ and vibration of C-OH at 1200–1020 cm⁻¹ were also observed. The peaks from products obtained from the reaction using either hierarchical Ni(0)/ZSM-5 or microporous Ni(0)/ZSM-5 as catalyst were looked similar. From the FTIR spectra, it could be suggested that the product is fumaric acid (HOOC-CH=CH-COOH), which is in accordance with the results observed in HPLC analysis. This product might be formed from a double carboxylation reaction of acetylene in the presence of magnesium halide (MgCl₂) as promoter [17].
4. Conclusions
The synthesis of microporous and hierarchical ZSM-5 zeolites followed by modification with nickel metal has been carried out. The catalysts were further used in the reaction of acetylene carboxylation with carbon dioxide targeted acrylic acid as product. HPLC analysis did not show the presence of acrylic acid in the reaction mixture. Alternatively, more polar compound such as fumaric acid may be produced.

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References
[1] Intergovernmental Panel on Climate Change (IPCC) 2014 Climate Change 2014:Synthesis Report ed R K Pachauri and L Meyer (Geneva: IPCC)
[2] Olah G A, Goepert A and Prakash G K S 2009 Beyond Oil and Gas: The Methanol Economy, 2 ed (Darmstadt: Wiley-VCH)
[3] Leung D Y C, Caramanna G and Maroto-Valer M M 2014 Renew. Sustain. Energy Rev. 39 426–43
[4] Sakakura T, Choi J C and Yasuda H 2007 Chem. Rev. 107 2365–87
[5] Wang X, Wang H and Sun Y 2017 Chem. 3 211–28
[6] Doi R, Abdullah I, Taniguchi T, Saito N and Sato Y 2017 Chem. Commun. 53 7720–3
[7] Al-Ghamdi M, Vummaleti S V C, Falivene L, Pasha F A, Beetstra D J and Cavallio L 2017 Organometallics 36 1107–12
[8] Krisnandi Y K, Putra B A P, Bahtiar M, Zahara, Abdullah I and Howe R F 2015 Procedia Chem. 14 508–15
[9] Krisnandi Y K, Samodro B A, Sihombing R and Howe R F 2015 Indonesian Journal of Chemistry 15 263–8
[10] Krisnandi Y K, Nurani D A, Agnes A, Pertwi R, Antra N F, Anggraeni A R, Azaria A P and Howe R F 2019 Indonesian Journal of Chemistry 19 115–23
[11] Zahara Z, Krisnandi Y K, Wibowo W, Nurani D A, Rahayu D U C and Haerudin H 2018 AIP Conf. Proc. 2023 020088
[12] Zhao Q N, Song Q W, Liu P, Zhang Q X, Gao J H and Zhang K 2017 Chinese J. Chem. 36 187–93
[13] Xie H, Lin T, Shi L and Meng X 2016 RSC Adv. 6 97285–92
[14] Wang L, Zhang Z, Yin C, Shan Z and Xiao F S 2010 Microporous Mesoporous Mater. 131 58–67
[15] Ziebro J, Łukasiewicz I, Borowiak-Palen E and Michalkiewicz B 2010 Nanotechnology 21 4960–3
[16] Yang J, Gioia A J D 2006 HPLC Determination of Free Acrylic Acid and Monomers in Polyacrylates (Milford: Waters Corporation) Application Note
[17] Fujihara T, Horimoto Y, Mizoe T, Sayyed F B, Tani Y, Terao J, Sakaki S and Tsuji Y 2014 Org. Lett. 16 4960–3

Figure 5. FTIR spectra of product from carboxylation of acetylene using (a) hierarchical, and (b) microporous Ni/ZSM-5 catalysts.