Selective Short Chain Carboxylic Acid Production over Fe:Zeolite Nanoparticles from CO₂ Hydrogenation Reaction

Nurazni Amat Bahari¹, Wan Nor Roslam Wan Isahak¹,²,*

¹Research Centre for Sustainable Process Technology, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.
²Chemical Engineering Programme, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

wannorroslam@ukm.edu.my

Abstract. In recent years, formic acid become as an alternative fuel that offer useful solution for the efficient energy storage. The formic acid was synthesized by the carbon dioxide hydrogenation reaction by using catalyst. The preliminary study on catalyst between zeolite that act as support while hematite iron oxide (α-Fe₂O₃) that act as co-catalyst produced a new composite which is Fe-Zeolite. The Fe-Zeolite was synthesized by using sol-gel method with a weight ratio of 1:2 and 2:2. 1:2 of Fe-Zeolite gives the good activity for the production of formic acid which is 1305.41 ppm. The presence of different support material such as zeolite and mesoporous silica nanoparticles (MSN) showed a significant difference in the catalytic performance and formic acid selectivity. The morphological and textural properties of the synthesized catalysts were determined by FTIR, XRD, TEM, and FESEM while the formation of formic acid from CO₂ hydrogenation reaction was evaluated using High Performance Liquid Chromatography (HPLC).

Introduction

Nowadays, the rising concentration of carbon dioxide (CO₂) gases in the atmosphere has attracted studies on the various causes of environmental problems, such as global warming, climate change, rising sea levels, and ozone depletion [1]. Researchers also strived to find ways to reduce the concentration of CO₂, and one such method is CO₂ hydrogenation, which has been considered as an effective and inexpensive technique [2].

Lower weight hydrocarbon (C₁–C₄) or oxygenated ones, such as carbon monoxide, methanol, formic acid, dimethyl ether, and so on, are products formed from the CO₂ hydrogenation reaction [3]. An efficient catalyst is needed to initiate the reaction, which can then break down the double bond of C=O resulting from the extreme thermodynamic and kinetic stability [4]. Hematite iron oxide (α-Fe₂O₃), a highly stable iron oxide, is a non-toxic material that has low production cost [5]. Meanwhile, zeolites are a group of crystalline aluminosilicates with group I or II elements as counter ions; these are also inexpensive materials that are abundant and readily available [6]. They consist of a [SiO₄]⁴⁻ and [AlO₄]³⁻ tetrahedral structure [7].

In the present study, we synthesized the composite Fe:Zeolite through the sol-gel method for the production of formic acid, under the consideration that α-Fe₂O₃ and zeolite both produce high catalytic activity. The effects of the weight ratio between the support and co-catalyst were investigated and the influence of the crystal size on the production of formic acid was also tested.
Materials and Method

Materials
Zeolite (Fluka BioChemika), iron nitrate nonahydrate (R&M), oxalic acid dihydrate (R&M), polyethylene glycol 2000 (Merck), absolute ethanol (99.8%, HmbG), 1,4-dioxane (Fisher Chemical), CO\textsubscript{2} (compressed, NIG Gases Sdn. Bhd), and purified H\textsubscript{2} (compressed, Linde Malaysia Sdn. Bhd) without further purification.

Synthesis of Fe-zeolite nanocomposite
The sol-gel method was used to synthesize the Fe:Zeolite nanocomposite, as described in Fig. 1. The zeolite and Fe (III) nitrate mixtures were prepared in ethanol with two weight ratios of 1:2 and 2:2. Zeolite was immersed in absolute ethanol with continuous stirring at 60 °C for 10 min. Then, Fe (III) nitrate was mixed into the solution and stirred continuously for another 10 min. To this, 1 mL of PEG was slowly added. Next, oxalic acid was mixed with absolute ethanol in another beaker with a magnetic stirrer at 50 °C for 10 min. The oxalic acid solution was poured slowly into a previous beaker under continuous stirring for 30 min until a gel was formed. Then, the gel produced was dried in an oven at 105 °C. Finally, further calcination was performed in the furnace at 400 °C for 2 h.

\[ \text{CO}_2 \text{ hydrogenation} \]
The activity to induce CO\textsubscript{2} hydrogenation to formic acid was performed in a low-pressure and low-temperature reactor made of a stainless steel chamber (~12.3 cm in length and 6.5 cm internal diameter) placed in an electrically heated oven. About 0.2 g of catalyst immersed in 35 mL of 1,4-dioxane was used as solvent for the reaction. After setting up the reactor, H\textsubscript{2} flushing was done for 1 min to remove air. Then, the CO\textsubscript{2} and H\textsubscript{2} gases were injected to the required pressure of 35 bar (initial pressure) with the ratio of 1:3.5, respectively. The reaction was conducted at a temperature of 130 °C for 6 h. The reactor was left overnight, after which the product was collected. Then, the pressure was carefully released. High-performance liquid chromatography (HPLC) was used to analyze the concentration of the generated formic acid.
Results and Discussion

Fourier-transform infrared spectroscopy (FTIR) analysis

The FTIR spectra for the pure zeolite 13x, the dried oxalates at 105 °C, and calcined catalysts at 400 °C are shown in Fig. 2. The pure zeolite 13x indicates a broad peak of O-H stretching at 3401 cm⁻¹ and a sharp peak of aluminosilicate group at 974 cm⁻¹. The formation of oxalates by the reaction of Fe precursors with oxalic acid, as shown in Fig. 2 (b). Furthermore, before calcination, a broad peak at ~3390–3493 cm⁻¹ is assigned to O-H stretching due to the moisture; as the temperature increases, the peak gradually decreases as shown in Fig. 2 (c). The strong stretching peak occurs at ~1668–1725 cm⁻¹ due to the C=O group, the peak at ~1404–1443 cm⁻¹ indicates the C-O group, and that at ~900–675 cm⁻¹ is for the vibration of C-H group. The peak at ~450–550 cm⁻¹ belongs to the Fe-O group. The final peak occurs at ~979–1047 cm⁻¹, which indicates the vibration of the aluminosilicate group in the Fe:Zeolite oxalates. After calcination, all the organic compounds were decomposed. The major changes in some of the peaks at high temperature prove the conversion from oxalates to oxide, as shown in Fig. 2 (c). Finally, the O-H stretching is weakened and indicates the ~957–976 cm⁻¹ vibration due to the aluminosilicate group from the Fe:Zeolite composite while those at 428 and 515 cm⁻¹ can be attributed to the Fe-O group from α-Fe₂O₃[8].

XRD analysis

The XRD pattern of α-Fe₂O₃, pure zeolite and Fe:Zeolite composite are shown in Fig. 3 without any detectable impurities. The characteristic 2θ peaks of α-Fe₂O₃ at 24.1°, 33.1°, 35.6°, 40.8°, 49.4°, 54.0°,
62.4°, and 63.9° correspond to the (012), (104), (110), (113), (024), (116), (214), and (300) planes, respectively. The characteristic 2θ peaks of zeolite and Fe:Zeolite at 6.1°, 9.9 °, 11.7°, 15.4°, 18.4°, 20.0°, 23.3°, 26.6° and 30.9° correspond to the (111), (220), (311), (331), (511), (440), (533), (642) and (751) planes, respectively. Table 1 and Table 2 shows their intensity, crystallite size, and crystallinity percentage on each plane; it also shows that pure zeolite gives the highest intensity and highest crystallinity at planar (111). As shown in the table, after modification, the intensity and crystallinity decreases as the weight ratio of Fe increases due to the absorption of Fe into the framework of zeolite [9].

![X-ray patterns](image)

**Fig. 3.** X-ray patterns of (a) α-Fe₃O₅ (b) Zeolite (c) 1:2 Fe-Zeolite (d) 2:2 Fe-Zeolite

| hkl  | 2θ (degree) | Crystallite size (nm) | Crystallinity (%) |
|------|-------------|-----------------------|------------------|
| 012  | 24.14       | 16.68                 | 82.5             |
| 104  | 33.16       | 16.04                 | 85.0             |
| 110  | 35.61       | 17.65                 | 85.4             |
| 113  | 40.85       | 19.00                 | 78.2             |
| 024  | 49.45       | 19.58                 | 88.8             |
| 116  | 54.08       | 14.36                 | 90.9             |
| 214  | 62.41       | 18.98                 | 67.2             |
| 300  | 63.96       | 22.04                 | 71.3             |
Table 2. Intensity, crystallite size and crystallinity percent of zeolite and composite Fe-zeolite nanoparticle form XRD analysis

| hkl  | 2θ  | Zeolite |  | 1:2 Fe-Zeolite |  | 2:2 Fe-Zeolite |
|------|-----|---------|---|----------------|---|----------------|
|      |     | Crystallite size (nm) | Crystallinity (%) | Crystallite size (nm) | Crystallinity (%) | Crystallite size (nm) | Crystallinity (%) |
| 111  | 6.10| 79.23   | 99.1 | 66.26          | 98.4 | 49.85          | 97.5 |
| 220  | 9.99| 85.44   | 95.9 | 71.93          | 86   | NA             | 81.6 |
| 311  | 11.73| 85.76  | 88.2 | 58.51          | 88.5 | NA             | 75.4 |
| 331  | 15.45| 83.93  | 95.7 | 53.99          | 93.8 | NA             | 92.5 |
| 511  | 18.43| 77.47  | 92.2 | 74.37          | 83.3 | NA             | 82.1 |
| 440  | 20.07| 81.28  | 96.3 | 55.65          | 84.2 | NA             | 58.5 |
| 533  | 23.34| 68.76  | 93.5 | 41.54          | 82.5 | 48.50          | 65.9 |
| 642  | 26.68| 74.74  | 94.7 | 41.74          | 72.9 | NA             | 57.6 |
| 751  | 30.97| 66.89  | 91.4 | 49.85          | 68.5 | NA             | 40.1 |

NA: not available

Surface morphology

The shape and size of the particle was evaluated using TEM under 60000 times magnification for the α-Fe₂O₃ image and 28000× magnification for the Fe:Zeolite image. Fig. 4 (a) indicates the pure α-Fe₂O₃ which shows a quasi-spherical shape and particle size around ~19–23 nm. Fig. 4 (b) shows the zeolite as a support layer for the Fe particle. Fig. 5 (a1, b1, c1) shows the results from FESEM under 50000× magnification for the α-Fe₂O₃ image and 1000× magnification for the zeolite and Fe:Zeolite images. As shown in Fig. 5 (a1), the α-Fe₂O₃ image indicates Fe in nanoparticle size. The pure zeolite in Fig. 5 (b1) indicates that they have an octahedral structure that is nearly orbicular, which is similar to a previously reported finding [10]. The Fe:Zeolite composite shown in Fig. 5 (c1) proves that the small Fe particles are agglomerated on the surface of zeolite.

Fig. 4. TEM images of (a) α-Fe₂O₃ (b) 1:2 Fe-Zeolite
Fig. 5. FESEM and EDX of (a1) α-Fe₂O₃, (b1) Zeolite and (c1) 1:2 Fe-Zeolite

Catalytic activity
Formic acid, as the main product of CO₂ hydrogenation, was analyzed using HPLC. Fig. 6 indicates the activity of the catalysts of several materials. As can be seen, α-Fe₂O₃ and zeolite present good results in terms of formic acid production at concentrations of 1091 and 494 ppm, respectively. In comparison, the Fe:Zeolite ratio of 1:2 yields higher formic acid production at a concentration of 1305 ppm. At a 2:2 ratio, it shows the declining formation of formic acid due to the higher content of Fe particles on the zeolite surface, resulting in a thicker layer and more agglomeration.

![Graph showing catalytic activity of various catalysts](image)

Fig. 6. Catalytic activity of various catalyst (note: MSN: Mesoporous silica nanoparticle)
Conclusions
In summary, the Fe:Zeolite composite was well synthesized through the sol-gel method under the following conditions: Fe:Zeolite weight ratio of 1:2, PEG volume of 1 mL, and calcination temperature of 400 °C. The method yields the highest concentration of formic acid (1305.41 ppm) compared with other catalysts. Zeolite showed higher formic acid production compared with mesoporous silica nanoparticles (MSN). Combination of Fe-zeolite catalysts gives highest formic acid production and selectivity at optimum parametric condition.

References
T. Witoon, J. Chalornthgiam, P. Dumrongbunditkul, M. Chareonpanich, J. Limtrakul, CO₂ hydrogenation to methanol over Cu/ZrO2 catalysts: Effects of zirconia phases, Chem. Eng. J. 293 (2016) 327–336. doi:10.1016/j.cej.2016.02.069.

X.L. Liang, X. Dong, G.D. Lin, H. Bin Zhang, Carbon nanotube-supported Pd-ZnO catalyst for hydrogenation of CO₂ to methanol, Appl. Catal. B Environ. 88 (2009) 315–322. doi:10.1016/j.apcatb.2008.11.018.

Y.H. Choi, Y.J. Jang, H. Park, W.Y. Kim, Y.H. Lee, S.H. Choi, J.S. Lee, Carbon dioxide Fischer-Tropsch synthesis: A new path to carbon-neutral fuels, Appl. Catal. B Environ. 202 (2016) 605–610. doi:10.1016/j.apcatb.2016.09.072.

C. Chiang, K. Lin, H. Chuang, C. Wu, Conversion of hydrogen / carbon dioxide into formic acid and methanol over Cu / CuCr₂O₄ catalyst, Int. J. Hydrogen Energy. (2017) 1–17. doi:10.1016/j.ijhydene.2017.04.226.

B. Alqasem, N. Yahya, S. Qureshi, M. Irfan, Z. Ur Rehman, H. Soleimani, The enhancement of the magnetic properties of α-Fe₂O₃ nanocatalyst using an external magnetic field for the production of green ammonia, Mater. Sci. Eng. B. 217 (2017) 49–62. doi:10.1016/j.mseb.2016.12.002.

M.N. Chong, Z.Y. Tneu, P.E. Poh, B. Jin, R. Aryal, Synthesis, characterisation and application of TiO₂-zeolite nanocomposites for the advanced treatment of industrial dye wastewater, J. Taiwan Inst. Chem. Eng. 50 (2015) 288–296. doi:10.1016/j.jtice.2014.12.013.

V. Garshasbi, M. Jahangiri, M. Anbia, Equilibrium CO₂ adsorption on zeolite 13X prepared from natural clays, Surf. Appl. Sci. 393 (2017) 225–233. doi:10.1016/j.surfsci.2016.09.161.

N.A. Bahari, W.N.R.W. Isakah, M.S. Masdar, M.M. Ba-Abbad, Optimization of the controllable crystal size of iron/zeolite nanocomposites using a Box-Behnken design and their catalytic activity, Appl. Nanosci. 9 (2019) 209-224. doi.org/10.1007/s13204-018-0920-8.

C. Ramakrishna, R. Krishna, T. Gopi, G. Swetha, B. Saini, S. Chandra Shekar, A. Srivastava, Complete oxidation of 1,4-dioxane over zeolite-13X-supported Fe catalysts in the presence of air, Cuihua Xuebao/Chinese J. Catal. 37 (2016) 240–249. doi:10.1016/S1872-2067(15)61030-0.

S.J. Chen, Y. Fu, Y.X. Huang, Z.C. Tao, M. Zhu, Experimental investigation of CO₂ separation by adsorption methods in natural gas purification, Appl. Energy. 179 (2016) 329–337. doi:10.1016/j.apenergy.2016.06.146.

Acknowledgements
The authors wish to thank Universiti Kebangsaan Malaysia (UKM) for funding this project under Research Grant, DIP-2018-021, and the Centre of Research and Innovation Management (CRIM) UKM for the use of the instruments.