A viable system for carbon dioxide (CO_2) methanation over fibrous silica ZSM-5 for substitute natural gas (SNG)

I Hussain¹, A A Jalil²*, N A A Fatah², M. Ibrahim², M S Azami¹, W Fadlun², M A H Aziz¹, HU Hambali²
¹ Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru
² School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
³ Centre of Hydrogen Energy, Institute of Future Energy, 81310 UTM Johor Bahru, Johor, Malaysia

*aishahaj@utm.my

Abstract. Catalytic CO_2 methanation offers an attractive and sustainable way for the production of substituted natural gas (SNG), which may be used as a clean alternative energy source than fossil fuels. A metal-free fibrous silica ZSM-5 catalyst (FS@ZSM-5) was synthesized via the microemulsion technique to conduct catalytic CO_2 methanation. The FESEM, BET, and FTIR characterization techniques were used to investigate the surface morphology, pore structure of the catalysts. It was noticed that the commercialized ZSM-5 showed 37% CH_4 selectivity with a rate of methane formation 0.067 mmol m^-2 s^-1. While FS@ZSM-5 exhibited high CH_4 selectivity of 66 % with rate of methane formation 0.108 mmol m^-2 s^-1 using same conditions (T = 500 ºC and GHSV = 36,000 mL h^-1 g^-1). Therefore, the FS@ZSM-5 was proved an efficient and active catalyst for CO_2 methanation activity.

1. Introduction
Climate change is the most contentious and aggravating issue of the 21st century due to greenhouse gases. Carbon dioxide (CO_2), an important greenhouse gas, has contributed much to increase the temperature of our earth planet. Therefore, the recycling of CO_2 has been the key strategy for researchers. The transformation of CO_2 into methane has fascinated substantial interest in recent years due to its high potential for commercialization. The CO/CO_2 methanation reaction was discovered by Sabatier and Senderens in 1902 [1, 2]. CO/CO_2 methanation reactions produce the methane is called substituted natural gas (SNG) and is considered one of the most important energy sources of the 21st century, especially in China, a country that does not have an abundant amount of natural gas [3, 4, 5]. There are many applications of SNG to produce useful products, such as carbon tetrachloride, methanol, and formates. Besides, SNG can also be used in gas turbines, gas engines, and the transportation sector, such as in vehicles. Besides, the existing storage tanks and pipelines infrastructures can be used for transportation SNG to long distances. [5, 6]. The CO_2 methanation is thermodynamically favorable (∆G_{298K} = -130.8 kJ/mol). For catalytic CO_2 methanation, an efficient, active, and thermally stable catalyst is required to convert CO_2 into CH_4. In the last decades, several studies have been conducted using different types of catalysts [1]. Pandey et al. conducted CO_2 methanation without using support, while, Hamid et al. performed CO_2 methanation without metal [7, 8]. Although several studies have been conducted to design suitable and active catalysts for CO_2 methanation. In spite of this, it is still a great
challenge to design a highly efficient and active catalyst for industrial applications due to exothermic nature and coke formation during CO\textsubscript{2} methanation, which are the major issues that may deactivate the catalysts. There are many studies about CO\textsubscript{2} methanation over metal-based catalysts, particularly on transition metals. However, the metal-free catalyst was rarely used in CO\textsubscript{2} methanation. Therefore, CO\textsubscript{2} methanation was conducted using metal-free fibrous silica ZSM-5. In recent times, our research group is active in synthesizing several types of fibrous materials, like KCC-1, discovered by Polystiwar in 2010, such as fibrous silica beta zeolite, fibrous silica mordenite, and fibrous silica TiO\textsubscript{2} and applied in different reactions like isomerization and Photocatalysis [9-13]. Based on the literature, there are very rare studies of CO\textsubscript{2} methanation over metal-free catalysts. Therefore in this present study, a metal-free fibrous silica ZSM5 catalyst was assessed for CO\textsubscript{2} methanation.

2. Experimental

2.1. Catalyst preparation

The microemulsion method was used to synthesize fibrous silica ZSM-5 using a similar to our previously reported protocol [13]. In a typical synthesis procedure, 3.2 g of urea and 9.3 g of cetyltrimethylammonium bromide (CTAB) were mixed together in 190 mL of distilled water and stirred for 20 min to make homogenize solution. 1-Butanol (7mL) and Toluene (130 mL) were added to this mixed solution as oil phase and co-surfactant, respectively. After 30 min stirring, commercial ZSM-5 zeolite seeds (Zeolyst international) were added, and then 10 mL of tetraethoxysilicate (TEOS) was mixed in a solution with 2 h stirring at room temperature. The solution was shifted into a Teflon bottle from the beaker to keep in oven for 4 h at 120 °C. The centrifugation of the mixture was performed at 4000 rpm to isolate the solid product, which was placed in the oven overnight at 120 °C. Finally, resulting solid material was calcined at 550 °C for 6 h and crushed into a fine powder, entitled “FS@ZSM-5”.

2.2. Characterization of catalysts

To examine the catalytic properties of both commercialized ZSM-5 and synthesized FS@ZSM catalysts, different characterizations techniques were used, such as field emission scanning electron microscopy (FESEM) was employed to execute morphology of the catalysts using Zeiss Supra VP35 instrument. The functional groups were studied by the FTIR-KBr method using an Agilent Cary 640 FTIR spectrometer. Besides, the pore size distribution was calculated by non-local density functional theory (NLDFT) methods. Prior to the analysis, the catalysts were degassed 1 h at 300 °C. Then BET surface area was calculated using a Beckman Coulter SA 3100 at 77 K.

2.3. Experimental setup for CO\textsubscript{2} methanation

Catalytic CO\textsubscript{2} methanation was performed in the range of 150-600 °C using a fixed-bed reactor, which was placed in a circular-shaped electric furnace. The catalysts were palletized and sieved first before filling the catalyst into the reactor tube. 200 mg of each catalyst was filled into the reactor tube. Prior to the catalytic performance, air treatment was performed for 1 h to remove the impurities from the surface of the catalyst. Then the reduction was performed for 3 h at H\textsubscript{2} = 20 ml/min to activate the catalysts. The temperature was adjusted and stabilized at 150 °C, and reactant gases were introduced into the column using H\textsubscript{2} /CO\textsubscript{2} = 4 :1, at 1 atmospheric temperature. Products formed during CO\textsubscript{2} methanation activity were monitored by online 7820 N Agilent (gas chromatograph). The CO\textsubscript{2} conversion, methane selectivity were measured by the following Eq. (1-4):

\[
\text{CO}_2 \text{ conversion } (\%) = \frac{M_{CH_4} + M_{CO_2}}{M_{CO} + M_{CH_4} + M_{CO_2}} \times 100
\]

\[
\text{CH}_4 \text{ selectivity } (\%) = \frac{M_{CH_4}}{M_{CH_4} + M_{CO_2}} \times 100
\]
\[
\text{CH}_4 \text{ yield (\%)} = \frac{X_{CO} \times S_{CH_4}}{100} \tag{3}
\]

\[
\text{Rate (mmol m}^{-2}\text{s}^{-1}) = \frac{M_{CH_4}}{S \times A \times \text{W}_{cat} \times S} \tag{4}
\]

3. Results and discussions

Figure 1 indicates the FESEM studies of as-synthesized FS@ZSM-5. It can be seen a round-shaped, spherical, and well-ordered microspheres particles, which look like cockscomb structures of uniform size particles of 100-200 nm. It will be a significant contribution to enhanced mesoporosity in FS@ZSM-5 due to this new morphology. A detailed study of the formation of mesopores will be conducted in the next section. It is suggested that the new morphology may improve the adsorption of \( \text{H}_2 \) and \( \text{CO}_2 \) molecules at the surface of FS@ZSM-5 during catalytic activity [14].

\[\text{Figure 1.} \] FESEM images of (A) ZSM-5, (B) FS@ZSM-5 and \( \text{N}_2 \) adsorption-desorption isotherm and NLDFT pore size distribution of (C) ZSM-5 and (D) FS@ZSM-5

Figures C-D presents the textural properties of the catalysts as it can be seen that a reversible type IV isotherm was illustrated by both commercialized ZSM-5 and synthesized FS@ZSM-5 catalysts. The adsorption of nitrogen in both catalysts at lower \( \text{P/P}_0 \) is due to micropore [8]. It should be noted that at
higher relative pressure, the nitrogen adsorption became more significant at \( P/P_0 = 0.4 \) and 0.9. It was due to intra- and interparticle pores, respectively. Compared to commercialized ZSM-5, the synthesized FS@ZSM-5 (Figure 1D) showed higher intra- and interparticle porosity. Therefore the FS@ZSM-5 demonstrated a tremendous increase in the BET Surface area (615 m\(^2\)/g) presented in Table 1. The main pore size distribution appeared in the range of 2-9 nm for ZSM-5 (Figure 1C). While the FS@ZSM-5 illustrated the main pore size distributions in the range of 2-10 nm, it was due to the self-assembling of CTAB molecules during the synthesis of catalysts. The large pores from 10 to 25 nm presented to the inter-fibers distance, which might contributed to increase the BET surface area [8, 14]. These results are consistent with the unique FESEM results.

| Catalyst   | \( S_{\text{BET}} \) (m\(^2\)/g) | Total pore Volume (cm\(^3\)/g) | Micropore volume (cm\(^3\)/g) | Mesopore volume (cm\(^3\)/g) |
|------------|---------------------------------|--------------------------------|------------------------------|-------------------------------|
| ZSM-5      | 257                             | 0.155                          | 0.092                        | 0.063                         |
| FS@ZSM-5   | 615                             | 0.488                          | 0.082                        | 0.406                         |

Figure 2 FTIR-KBr spectra of for commercialized ZSM-5 (blue line) and synthesized FS@ZSM-5 (red line)

Figure 2 presents the FTIR-KBr spectra of ZSM-5 and FS@ZSM-5 were performed in the range of 4000 to 400 cm\(^{-1}\). Both catalysts presented an intense band at 3445 cm\(^{-1}\), assigned to hydroxyl groups due to water molecules at the surface of catalysts. The band appeared at 1635 cm\(^{-1}\) indicates the deformational vibrations of water molecules. Whereas, the bands at 1220 cm\(^{-1}\) and 1097 cm\(^{-1}\) show the internal-external and asymmetric stretching of the siloxane groups [14]. The band at 965 cm\(^{-1}\) presents the surface hydroxyl groups, which confirmed the fibrous morphology of FS@ZSM-5; similar results were reported by Mariam et al. 2019 [13]. A band appeared at 792 cm\(^{-1}\) due to the symmetric stretching of the siloxane groups on the surfaces of the catalyst. The bands at 543 cm\(^{-1}\) and 450 cm\(^{-1}\) illustrated the internal flexions of the tetrahedrons and five-membered rings, respectively [14].
Figure 3 describes the catalytic CO$_2$ methanation performance over both commercialized ZSM-5 (Figure 3A) and synthesized FS@ZSM-5 (Figure 3B). As it can be noticed that CH$_4$ selectivity and rate of methane formation were not significant for both catalysts at low temperatures. It might be due to that the activation energy was not enough to dissociate CO$_2$ and H$_2$ energy. However, on increasing the temperature, the CO$_2$ methanation catalytic activity for both catalysts increased significantly. It should be noted that the FS@ZSM-5 showed higher performance compared to ZSM-5 due to its unique morphology. The commercialized ZSM-5 illustrated 37% CH$_4$ selectivity with the rate of formation of methane 0.067 mmol m$^{-2}$s$^{-1}$. While the synthesized FS@ZSM-5 presented 66% CH$_4$ selectivity with rate of formation of methane 0.108 mmol m$^{-2}$s$^{-1}$ at T = 500 ºC and GHSV = 36,000 mL h$^{-1}$ g$^{-1}$. It should be noted that after 500 ºC, the system attained an equilibrium and several side reactions occurred, and the rate of methane formation and CH$_4$ selectivity lowered significantly, which is consistent with theoretical calculations of CO$_2$ methanation [14].

In most cases, the catalytic CO$_2$ methanation is performed over metal-based catalysts. Nevertheless, in the present study, CO$_2$ methanation activity was conducted on metal-free synthesized FS@ZSM-5, which led to the activation of H$_2$ and CO$_2$ molecules to form methane. A similar study was conducted on metal-free KCC-1 to perform CO$_2$ methanation, where high surface area and intra-inter particles, high basicity increased the CO$_2$ methanation activity. In another CO$_2$ methanation study, it was reported that the role of interparticle pores in Au/MCM, which increased the activity in terms of CO conversion [8]. Based on the catalytic properties of synthesized FS@ZSM-5, it is proposed that the high catalytic activity of synthesized FS@ZSM-5 was due to the new morphology after modification of commercialized ZSM-5. The formation of both intra- and inter-particles in synthesized FS@ZSM5, added to high surface area and the high basicity, which assisted the transportation of CO$_2$ and H$_2$ and molecules during the catalytic reaction [15-16].

**Figure 3.** Illustrates the catalytic performance for both ZSM-5 and FS@ZSM-5 catalysts (Figure 4A) for the CH$_4$ selectivity and rate of CH$_4$ formation (Figure 4B).

### 4. Conclusion

A metal-free fibrous silica ZSM-5 (FS@ZSM-5) was synthesized successfully via the microemulsion system to conduct catalytic CO$_2$ methanation. It was found that synthesized FS@ZSM-5 was proved a better catalyst in catalytic performance during CO$_2$ methanation activity due to its new morphology with surface area and the existence of both intra- and inter-particles distances. This study presents a new perspective of heterogeneous catalysis to clarify CO methanation’s applications. The encouraging
results of this study may provide a piece of useful information and findings to design a suitable catalyst in CO₂ methanation that can further consider being commercialized in producing SNG.

Acknowledgments
This research work was sponsored and supported by Universiti Teknologi Malaysia through Research University through UTM Transdisciplinary Grant No. 06G53.

References
[1] Bukhari S N, Chong C C, Teh L P, Veit D V, Ainirazali N, Triwahyono S and Jalil A A, Setiabudi H D 2019 Int. J. Hydrog. Energy. 44 (37) pp 20792-20804
[2] Liu S S, Jin Y Y, Yahong H, Jinxian Z and Ren J 2018 Fuel Process Technol 177 (274) pp 266-274
[3] Shuangshuang L, Honggui T, Dandan G, Zhi M and Yuan L 2017 Catal. Today 297(298) pp 298-307
[4] Jun R, Haidong L, Yongyong J, Jiuy Z, Shusen L, Jianying L and Zhong L 2017 Appl. Catal. B Environ. 201(561) pp 561-572
[5] Hussain I, Jalil, A A, Mamat, C R., Siang, T J, Azami, M S and Hambali, H U 2019 Journal of Energy and Safety Technology (JEST) 2(1) pp 15-19
[6] Garbarino G, Wang C, Cavattoni T, Finocchio E, Riani P, Stephanopoulos F M and Busca G 2019 Appl. Catal. B Environ. 248 pp 286–297
[7] Frontera P, Macario A, Ferraro M and Antonucci P 2017 Catalysts 7(2) pp 59
[8] Hamid MYS, Firmansyah M L, Triwahyono S, Jalil A A, Muktid R R, Feibriyanti E, Suendod V, Setiabudi H D, Mohamed M and Nabgan W 2017 Appl Catal. A: Gen. 532, 86 pp 86-94
[9] Polshettiwar V, Cha D, Zhang X and Basset J M 2010 Angew. Chemie - Int. Ed, 49, 9652-9656
[10] Ghani N N M, Jalil A A, Triwahyono S, Aziz M A A, A F A Rahman, M Y S Hamid, S M Izan, and Nawawi M G M 2019 Chem. Eng. Sci. 193, pp 217-229
[11] Hambali H U, Jalil A A, Siang T J, Abdulrasheed A A, Fatah N A. A, Hussain I, Azami M S 2019 Journal of Energy and Safety Technology (JEST) 2(1) pp 09-13.
[12] Ghani N N M, Jalil, A A Triwahyono S, Aziz M A A, Rahman A F A, Hamid M Y S, Izan S M
[13] M.G.M. Nawawi 2019 Chem. Eng. Sci. (193) pp 217-229.
[14] Ibrahim M, Jalil A A, Khusnun N F, Fatah N A A Int. J. Hydrog. Energy. 2019, https://doi.org/10.1016/j.ijhydene.2019.04.067
[15] Hussaina I, Jalilah A A, Mamat C R, Siang T J, Rahman A F A, Azami M S and Adnan R H 2019 Energy Convers and management 199 pp 112056.
[16] Aziz M A A, Jalil A A, Triwahyono S, Muktid R R, Taufiq-Y Y H and Sazegar M R 2014 Appl. Catal. B: Environ. 147 pp 359-368
[17] Aziz M A A, Jalil A A, Triwahyono S, Sidik S M 2014 Appl. Catal. A: Gen. 486 pp 115-122