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A viable system for carbon dioxide (CO₂) methanation over fibrous silica ZSM-5 for substitute natural gas (SNG)

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Abstract. Catalytic CO₂ 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 CO₂ 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% CH₄ selectivity with a rate of methane formation 0.067 mmol m⁻²s⁻¹. While FS@ZSM-5 exhibited high CH₄ selectivity of 66 % with rate of methane formation 0.108 mmol m⁻²s⁻¹ using same conditions (T = 500 °C and GHSV = 36,000 mL h⁻¹ g⁻¹). Therefore, the FS@ZSM-5 was proved an efficient and active catalyst for CO₂ methanation activity.

1. Introduction

Climate change is the most contentious and aggravating issue of the 21st century due to greenhouse gases. Carbon dioxide (CO₂), an important greenhouse gas, has contributed much to increase the temperature of our earth planet. Therefore, the recycling of CO₂ has been the key strategy for researchers. The transformation of CO₂ into methane has fascinated substantial interest in recent years due to its high potential for commercialization. The CO/CO₂ methanation reaction was discovered by Sabatier and Senderens in 1902 [1, 2]. CO/CO₂ 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 CO₂ methanation is thermodynamically favorable ($\Delta G_{298K} = -130.8$ kJ/mol). For catalytic CO₂ methanation, an efficient, active, and thermally stable catalyst is required to convert CO₂ into CH₄. In the last decades, several studies have been conducted using different types of catalysts [1]. Pandey et al. conducted CO₂ methanation without using support, while, Hamid et al. performed CO₂ methanation without metal [7, 8]. Although several studies have been conducted to design suitable and active catalysts for CO₂ 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 CO₂ methanation, which are the major issues that may deactivate the catalysts. There are many studies about CO₂ methanation over metal-based catalysts, particularly on transition metals. However, the metal-free catalyst was rarely used in CO₂ methanation. Therefore, CO₂ 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 TiO₂ and applied in different reactions like isomerization and Photocatalysis [9-13]. Based on the literature, there are very rare studies of CO₂ methanation over metal-free catalysts. Therefore in this present study, a metal-free fibrous silica ZSM5 catalyst was assessed for CO₂ 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 tetraethylorthosilicate (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 CO₂ methanation

Catalytic CO₂ 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 H₂ = 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 H₂ /CO₂ = 4 :1, at 1 atmospheric temperature. Products formed during CO₂ methanation activity were monitored by online 7820 N Agilent (gas chromatograph). The CO₂ conversion, methane selectivity were measured by the following Eq. (1-4):

$$\text{CO}_2 \text{ conversion (\%)} = \frac{M_{\text{CH}_4} + M_{\text{CO}_2}}{M_{\text{CO}} + M_{\text{CH}_4} + M_{\text{CO}_2}} \times 100 \quad (1)$$

$$\text{CH}_4 \text{ selectivity (\%)} = \frac{M_{\text{CH}_4}}{M_{\text{CH}_4} + M_{\text{CO}_2}} \times 100 \quad (2)$$

$$\text{CH}_4 \text{ yield (\%)} = \frac{X_{\text{CO}} \times S_{\text{CH}_4}}{100} \quad (3)$$

$$\text{Rate (mmol m}^{-2}\text{s}^{-1}\text{)} = \frac{M_{\text{CH}_4}}{S.A \times W_{\text{cat}} \times s} \quad (4)$$

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 H₂ and CO₂ molecules at the surface of FS@ZSM-5 during catalytic activity [14].

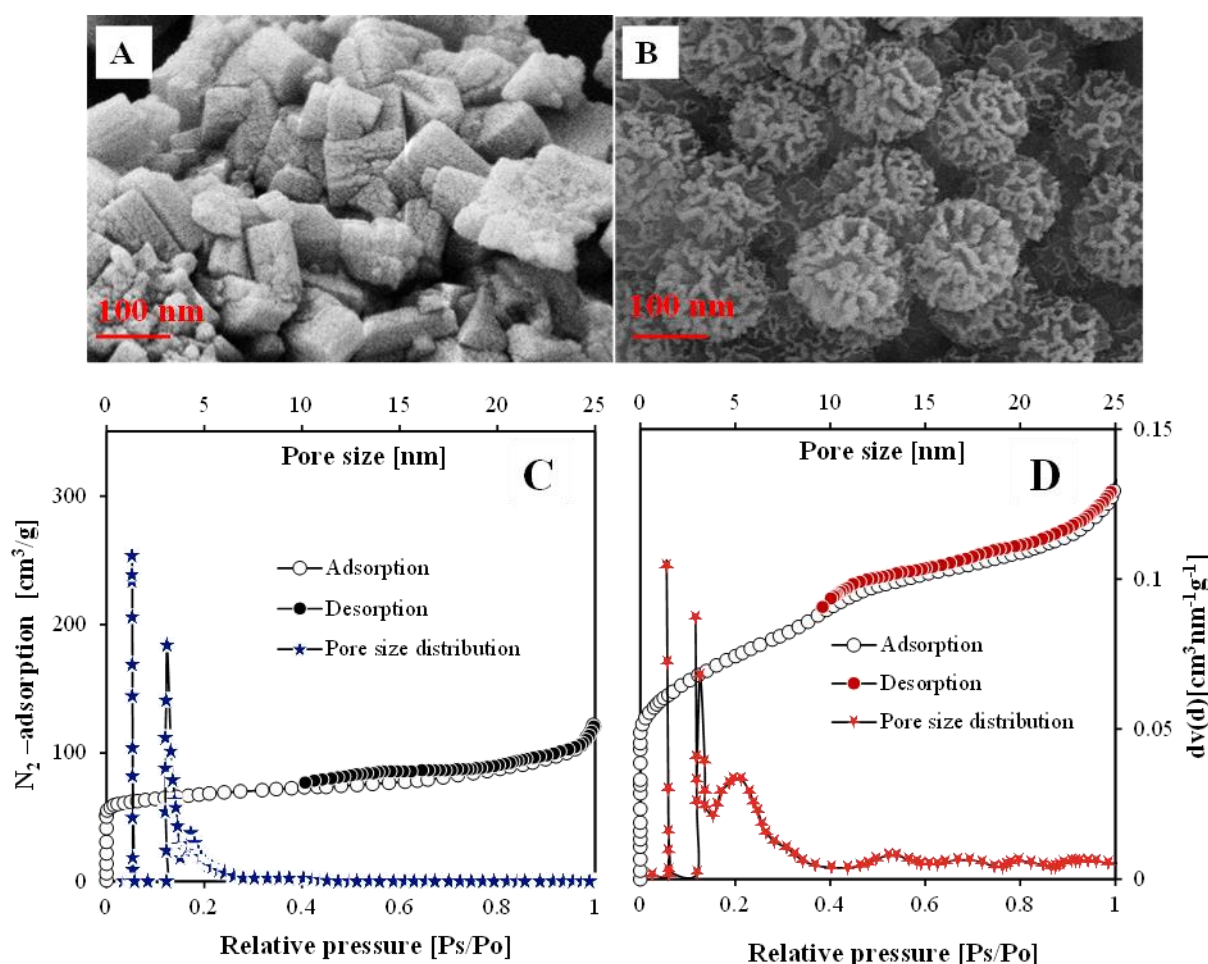


Figure 1. FESEM images of (A) ZSM-5, (B) FS@ZSM-5 and N₂ adsorption-desorption isotherm and NLDFT pore size distribution of (C) ZSM-5 and (D) FS@ZSM-5

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 P/P₀ 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 ($615 \text{ m}^2/\text{g}$) 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.

Table 1. Physicochemical properties of catalysts.

Catalyst	S_{BET} (m^2g^{-1})	Total pore Volume (cm^3g^{-1})	Micropore volume (cm^3g^{-1})	Mesopore volume (cm^3g^{-1})
ZSM-5	257	0.155	0.092	0.063
FS@ZSM-5	615	0.488	0.082	0.406

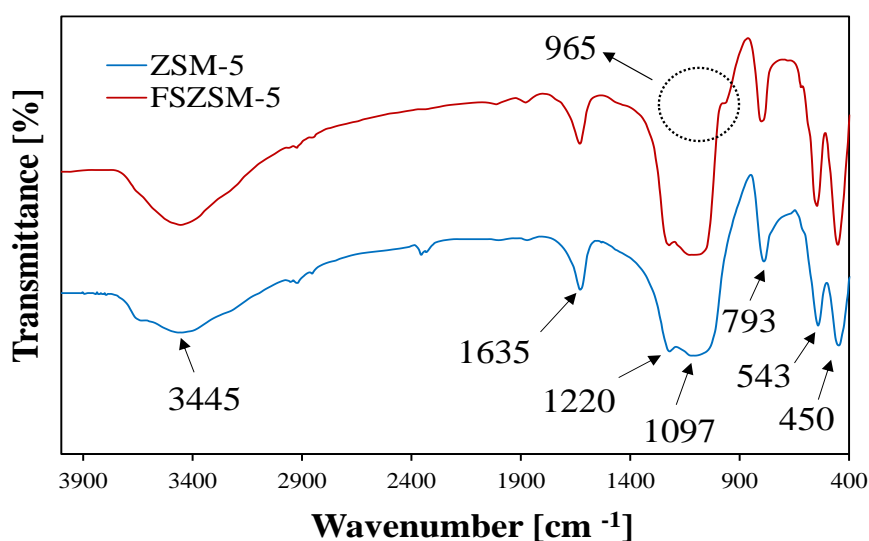


Figure 2 FTIR-KBr spectra of for commercialized ZSM-5 (blue line) and synthesized FS@ZSM-5 (red line)

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 CO₂ methanation performance over both commercialized ZSM-5 (Figure 3A) and synthesized FS@ZSM-5 (Figure 3B). As it can be noticed that CH₄ 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 CO₂ and H₂ energy. However, on increasing the temperature, the CO₂ 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% CH₄ selectivity with the rate of formation of methane 0.067 mmol m⁻²s⁻¹. While the synthesized FS@ZSM-5 presented 66 % CH₄ selectivity with rate of formation of methane 0.108 mmol m⁻²s⁻¹ at T = 500 °C and GHSV = 36,000 mL h⁻¹ g⁻¹. It should be noted that after 500 °C, the system attained an equilibrium and several side reactions occurred, and the rate of methane formation and CH₄ selectivity lowered significantly, which is consistent with theoretical calculations of CO₂ methanation [14].

In most cases, the catalytic CO₂ methanation is performed over metal-based catalysts. Nevertheless, in the present study, CO₂ methanation activity was conducted on metal-free synthesized FS@ZSM-5, which led to the activation of H₂ and CO₂ molecules to form methane. A similar study was conducted on metal-free KCC-1 to perform CO₂ methanation, where high surface area and intra-inter particles, high basicity increased the CO₂ methanation activity. In another CO₂ 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 CO₂ and H₂ and molecules during the catalytic reaction [15-16].

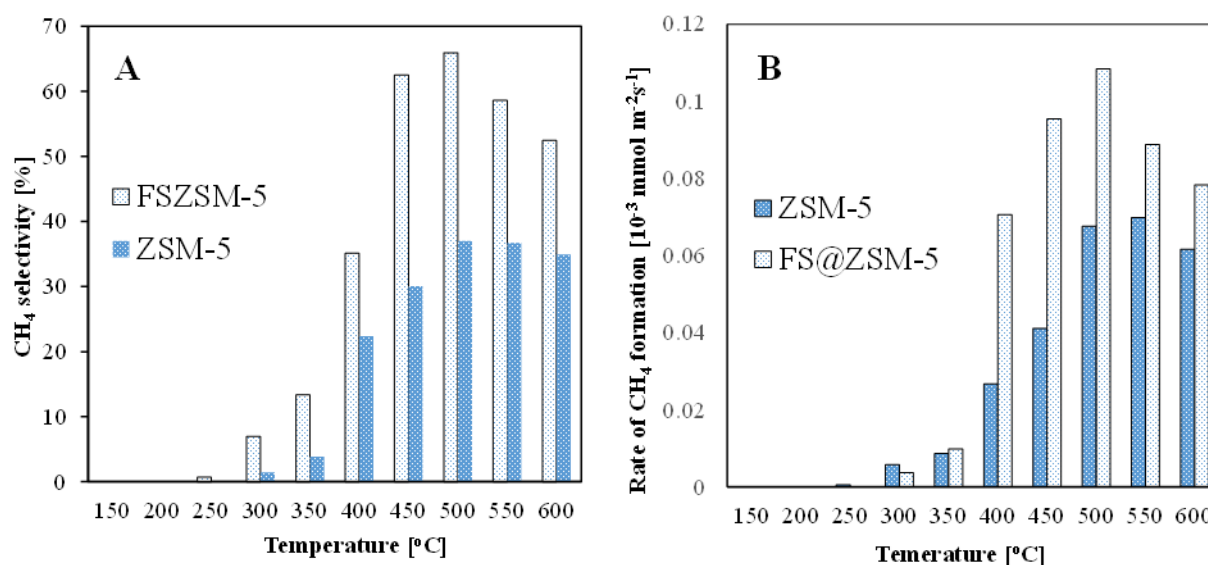


Figure 3. illustrates the catalytic performance for both ZSM-5 and FS@ZSM-5 catalysts (Figure 4A) for the CH₄ selectivity and rate of CH₄ formation (Figure 4B)

4. Conclusion

A metal-free fibrous silica ZSM-5 (FS@ZSM-5) was synthesized successfully via the microemulsion system to conduct catalytic CO₂ methanation. It was found that synthesized FS@ZSM-5 was proved a better catalyst in catalytic performance during CO₂ 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

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