

# Fabrication and characterization of highly active fibrous silica-mordenite (FS@SiO<sub>2</sub>-MOR) cockscomb shaped catalyst for enhanced CO<sub>2</sub> methanation

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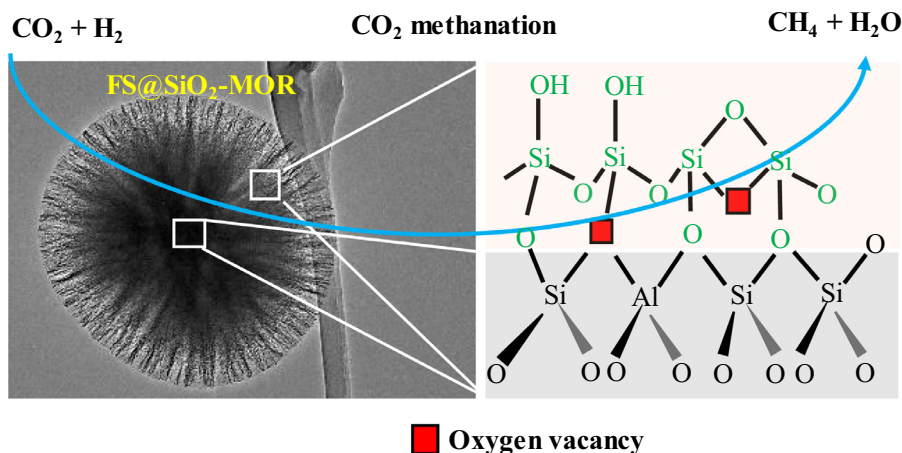
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## HIGHLIGHTS

- Fibrous silica-mordenite (FS@SiO<sub>2</sub>-MOR) catalyst was prepared by microemulsion.
- FS@SiO<sub>2</sub>-MOR exhibited CH<sub>4</sub> selectivity (68%) and CO<sub>2</sub> conversion (65%) at 500 °C.
- High activity was due to the high surface area, basicity and oxygen vacancies.
- Fibrous morphology of FS@SiO<sub>2</sub>-MOR suppressed coke deposition during CO<sub>2</sub> methanation.
- Carbonyls and linear CO<sub>2</sub><sup>\*</sup> were essential intermediates during CO<sub>2</sub> methanation.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Carbon dioxide (CO<sub>2</sub>) emissions are of global concern because of climate change. CO<sub>2</sub> methanation is one of the most prestigious technologies to convert CO<sub>2</sub> into value-added products such as substitute natural gas. In this study, a highly active fibrous silica-mordenite (FS@SiO<sub>2</sub>-MOR) catalyst has been synthesized by a microemulsion process and characterized by XRD, TEM, FESEM, N<sub>2</sub> adsorption analysis, FTIR-pyrrole, CO<sub>2</sub>-TPD, and ESR spectroscopy. The CO<sub>2</sub> methanation reaction was performed, and it was found that the FS@SiO<sub>2</sub>-MOR catalyst exhibited higher CH<sub>4</sub> selectivity (68%) and CO<sub>2</sub> conversion (65%) due to the distinctive fibrous morphology, which provided higher surface area, basic sites, and oxygen vacancies. In addition, the synthesized FS@SiO<sub>2</sub>-MOR catalyst exhibited high thermal stability (50 h) and significantly suppressed coke deposition compared to commercial mordenite. According to in-situ FTIR observations, the carbonyls and linear CO<sub>2</sub><sup>\*</sup> were the essential intermediates species for the formation of methane during CO<sub>2</sub> methanation via an associative mechanism.

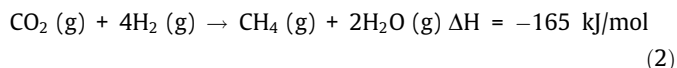
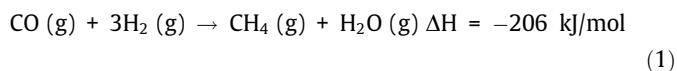
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## 1. Introduction

The consumption of fossil fuels (coal, oil, and natural gas) has increased since the industrial revolution due to recent advancements in human society. Therefore, tons of carbon dioxide (CO<sub>2</sub>) have entered the earth's atmosphere, causing climate change and global warming. As a result, our planet Earth has been facing several issues, including floods, droughts, transfer of diseases, the melting of glaciers, and a rise in temperature. There is a highly urgent need to control atmospheric CO<sub>2</sub> for our future generations (Sanz-Perez et al., 2016; Zhang et al., 2020; Hamid et al., 2019; Fatah et al., 2019). Recently, various strategies have been designed to control atmospheric CO<sub>2</sub>, including capturing, storing, and utilizing CO<sub>2</sub> by producing several useful chemicals, such as formate, methanol, methane, and ethanol. Methane has been produced by chemical conversion of CO/CO<sub>2</sub> and renewable hydrogen (H<sub>2</sub>) via the methanation reaction discovered by Paul Sabatier and Jean-Baptiste Senderens in 1902 (Eqs. (1) and (2)) (Hamid et al., 2019; Fatah et al., 2019; Mohanakrishna et al., 2018; Bai et al., 2017; Shahul Hamid et al., 2018; Hussain et al., 2020). Methane produced by methanation reactions is called substitute natural gas (SNG), which could replace natural gas in various sectors. SNG has been attracting much attention due to its environmentally-friendly nature and high calorific value. Noticeably, many countries, including Japan, China, and most European Union countries, have started the production of SNG to avoid the adverse environmental impacts of coal consumption. Compared to hydrogen, SNG can be stored and distributed without additional expenses due to the existing infrastructure, including storage facilities, filling stations, and pipeline networks (Frontera et al., 2017; Hussain et al., 2019; Lars and Jorg, 2015; Hussain et al., 2020).



Thermodynamically, CO<sub>2</sub> methanation is an exothermic reaction and feasible at low temperatures. However, according to chemical kinetics, there is a high kinetic energy barrier in the conversion of CO<sub>2</sub> (fully oxidized carbon with +4) to CH<sub>4</sub> (fully reduced carbon with -4) (Brooks et al., 2007; Park and McFarland, 2009; Gao et al., 2012). Regardless of the thermodynamically-favored CO<sub>2</sub> methanation process at low temperatures, the presence of a highly active and efficient catalyst is essential to lower the kinetic energy barrier in the chemical conversion of CO<sub>2</sub> to methane at an appropriate rate. During the CO<sub>2</sub> methanation reaction, much heat is generated ( $\Delta H = -165 \text{ kJ/mol}$ ), which creates hotspots in the reactor plants and causes deactivation of the catalysts. Furthermore, carbon deposition (coke formation) occurs via unwanted side reactions during CO<sub>2</sub> methanation, which could cause a significant decrease in catalytic activity by blocking the pores and active sites of the catalysts. To solve these issues, numerous research works have been reported for CO<sub>2</sub> methanation using different supports, including TiO<sub>2</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and zeolite (Qin et al., 2019; Ma et al., 2019; Lee et al., 2019; Tada et al., 2019; Lim et al., 2016; Feng et al., 2014; Azzolina-Jury et al., 2017). Nickel-promoted catalysts are used conventionally in CO<sub>2</sub> methanation due to their high activity and easy availability. However, high coke deposition and rapid deactivation are their main limitations. On the other hand, noble metals-promoted catalysts, mainly ruthenium-based catalysts, are considered an auspicious choice for CO<sub>2</sub> methanation. Nevertheless, these catalysts are not suitable for industrial-scale processes due to their economic viability (Italiano et al., 2020; Cardenas-Arenas et al., 2019).

The best choice for an efficient and suitable catalyst has been, and still remains, a great challenge. Therefore, further studies are needed to design a competitive catalyst for enhanced CO<sub>2</sub> methanation. Another aspect of catalytic CO<sub>2</sub> methanation is the mechanistic pathway of the reaction, which has always attracted much attention. Several types of studies have been executed to elucidate the mechanistic pathway of the CO<sub>2</sub> methanation reaction. According to literature, the CO<sub>2</sub> methanation mechanisms are categorized into two types, namely, the associative and dissociative mechanism. The associative mechanism involves associative adsorption of CO<sub>2</sub> and H<sub>2</sub> via formates or carbonates, which are converted to methane by hydrogenation. In the dissociative mechanism, the CO<sub>2</sub> dissociates directly into CO and O, which are adsorbed onto the surface of the catalyst. Then the adsorbed CO is dissociated into adsorbed C, which is subsequently hydrogenated to form methane (Su et al., 2016; Miao et al., 2016). Although several studies of CO<sub>2</sub> methanation reaction mechanisms have investigated different catalytic systems, the exact mechanistic pathway of the reaction is still under debate. Therefore, further studies are required to elucidate the reaction mechanism of CO<sub>2</sub> methanation.

In recent times, Polshettiwar reported a new material, fibrous silica KCC-1 nanospheres (KAUST Catalysis Center-1) (Polshettiwar et al., 2010), which showed a large surface area and high pore volume. Motivated by the unique fibrous morphology of KCC-1, we have synthesized different types of fibrous materials and effectively applied them in various reactions, including dry reforming of methane, CO methanation, and toluene methylation (Fatah et al., 2020; Hambali et al., 2020; Hussain et al., 2020; Ghani et al., 2019). In the present work, for the first time, we have synthesized a mesoporous fibrous silica-mordenite (FS@SiO<sub>2</sub>-MOR) catalyst through the microemulsion method in order to conduct CO<sub>2</sub> methanation. To our knowledge, this is the first report on CO<sub>2</sub> methanation using FS@SiO<sub>2</sub>-MOR as a metal-free catalyst. The prepared FS@SiO<sub>2</sub>-MOR catalyst exhibited a superior catalytic activity in terms of high CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity, with excellent thermal stability. Different characterization techniques, including field-emission scanning electron microscopy (FESEM), transmission electron spectroscopy (TEM), N<sub>2</sub> adsorption-desorption, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR-KBr and FTIR-pyrrole), CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD), and electron spin resonance (ESR) spectroscopy techniques were used to study the catalytic properties of FS@SiO<sub>2</sub>-MOR and commercial mordenite (MOR). Additionally, the possible mechanism of the CO<sub>2</sub> methanation reaction has been executed over synthesized FS@SiO<sub>2</sub>-MOR using an in-situ FTIR spectroscopy technique.

## 2. Experimental

### 2.1. Preparation of fibrous silica-mordenite (FS@SiO<sub>2</sub>-MOR)

To synthesize the fibrous silica-mordenite (FS@SiO<sub>2</sub>-MOR), commercial mordenite zeolite (Si/Al = 20, CBV 21A, Zeolyst International) was used as the seeds, using the microemulsion technique similar to our previous protocol (Ghani et al., 2019). Urea (3.5 g) and cetyltrimethylammonium bromide (CTAB; 9.7 g) were simultaneously dissolved in deionized H<sub>2</sub>O (200 mL) using a 500 mL glass beaker. After continuous vigorous stirring for 25 min, toluene and 1-butanol (125 mL and 8 mL, respectively) were added and the resulting solution was stirred again, for 35 min. The commercial mordenite seeds were added during continuous stirring. After complete mixing (when the color was milky white), tetraethylorthosilicate (TEOS; 10.5 mL) was added to the solution mixture as a silica source, with the stirring process continued for 3 h. For the pre-aging process, the solution mixture was

moved from a beaker into a Teflon bottle (500 mL), which was kept in the oven for 6 h at 120 °C. After centrifugation, the solid product was separated from the solution mixture and washed with acetone. Then, the solid product obtained was again placed in the oven for 12 h at 120 °C. Finally, the required solid product was crushed into fine powder and calcined in an electric furnace for 6 h at 550 °C, with a ramping rate of 3 °C/min. The synthesized catalyst and commercial mordenite were denoted as “FS@SiO<sub>2</sub>-MOR” and “MOR”, respectively.

## 2.2. Characterizations of the catalysts

The catalysts were subsequently subjected to various characterizations, such as XRD using a Bruker advance D8 diffractometer, which was connected with 40 mA and a Cu K $\alpha$  radiation source of 40 kV. The X-ray patterns were recorded between 0 and 90° at a 2 $\theta$  angle with a scanning speed of 1.50° min<sup>-1</sup>.

A Beckman Coulter SA 3100 analyzer was employed to examine the surface areas from N<sub>2</sub> adsorption–desorption at –196 °C. First, the samples were carefully degassed at 300 °C for 1 h under a high vacuum. Then, the nitrogen adsorption–desorption measurements were conducted for both degassed catalysts at –196 °C (liquid nitrogen temperature).

To analyze the morphological behavior of the catalysts, FESEM was executed by instrument brand no. JEOL JSM-6701F. To further study the morphological features of both catalysts, TEM was employed using a JEOL JEM-2100F TEM instrument. Before scanning the catalysts, an ultrasonication process was performed to disperse the catalysts in acetone before being deposited and dried on a copper grid.

FTIR was performed on the catalysts to study the functional groups, using the KBr method in the range of 4000–400 cm<sup>-1</sup> using an Agilent Cary 640 FTIR Spectrometer. Pyrrole-FTIR spectroscopy was carried out to characterize the basic properties of the catalysts. The pyrrole can be used as a probe molecule to detect the basicity in the catalysts through hydrogen bonding between positive hydrogen of pyrrole and the Lewis basic oxygen atoms of the silicate framework of the catalysts. The catalysts were activated at 400 °C in an in-situ FTIR stainless steel cell, which contained CaF<sub>2</sub> windows on each side. Then, both MOR and FS@SiO<sub>2</sub>-MOR catalysts were exposed to pyrrole (4 torrs) at room temperature (25 °C) for 15 min to adsorb the pyrrole molecules, and the FTIR spectra were obtained at 25 °C. In addition, the FTIR spectra were obtained after desorption of pyrrole at different temperatures (25 °C, 50 °C, 100 °C, 150 °C, and 200 °C).

To further examine the basicity of the catalysts, a Micromeritics Chemisorb-2720 chemisorption analyzer was used to study CO<sub>2</sub>-TPD profiles. First, the catalysts (25 mg) were treated in helium (25 mL min<sup>-1</sup>) for 1 h at 300 °C to remove moisture and other impurities. Then, the CO<sub>2</sub> adsorption process was conducted by exposing the catalysts to CO<sub>2</sub> using a stream of 25 mL/min for 30 min at 25 °C. The catalysts were then flushed with helium again until the thermal conductivity detector (TCD) signals were stable. Finally, the catalysts were heated in the presence of a helium stream (25 mL/min) between 30 °C and 850 °C, with a ramping rate of 10 °C/min, to obtain the CO<sub>2</sub>-TPD profiles.

ESR analysis was carried out to study oxygen vacancies and unpaired electrons using a JEOL JES-FA100 ESR spectrometer. Before the measurements, the catalysts were carefully degassed (1 h) and reduced (2 h) in an ESR test tube at 400 °C.

For in-situ FTIR spectroscopy to study the reaction mechanism of CO<sub>2</sub> methanation, the FS@SiO<sub>2</sub>-MOR was degassed (1 h) and reduced (2 h) at 400 °C in an in-situ FTIR stainless steel cell. Then, the FS@SiO<sub>2</sub>-MOR catalyst was exposed to CO<sub>2</sub> (20 torrs) and H<sub>2</sub> (80 torrs) at room temperature, and the FTIR spectra were recorded between 25 °C and 350 °C.

## 2.3. Experimental setup for CO<sub>2</sub> methanation

The catalytic CO<sub>2</sub> methanation was performed in a tubular fixed-bed reactor of 33 cm length with 0.8 cm internal diameter, connected vertically to an electric furnace. A complete schematic setup for the experimental CO<sub>2</sub> methanation has been depicted in Fig. 1. Typically, 200 mg of each catalyst was pelletized and sieved (40–60 mesh) to place it in the reactor tube. Before performing the CO<sub>2</sub> methanation activity, the catalysts were subjected to air (20 mL/min) and hydrogen (20 mL/min) treatment for 1 h and 3 h at 500 °C, respectively. To start the CO<sub>2</sub> methanation activity, the reaction temperature was fixed at a starting reaction temperature of 150 °C. Then, the reactant gas mixture with gas hourly space velocity of 45000 mL/g h (GHSV) was fed into the reactor system using a stoichiometric ratio of H<sub>2</sub>/CO<sub>2</sub> = 4:1 and pressure = 0.1 MPa. The catalytic performance was carried out in the range of 250–500 °C with 50 °C intervals. The quantitative analysis of the effluents was conducted by an Agilent 7820 N Gas Chromatograph (GC), which was coupled online to the TCD system and a GS-Carbon PLOT column (30 m  $\times$  0.32 mm ID  $\times$  3.0  $\mu$ m). A moisture trap was installed in the TCD system to avoid water inflow to the GC. The gas lines in the setup consisted of 1/4" and 1/8" stainless tubing fitted with Swagelok connectors. The GC oven was held at 250 °C during the analysis. The signals generated from the TCD were made readable with Clarity<sup>®</sup> software. High purity N<sub>2</sub> (flow rate 30 mL min<sup>-1</sup>) was used as the carrier gas to observe the amounts of CH<sub>4</sub>, CO, and remaining CO<sub>2</sub>. The following equations (Eqs. (3)–(6)) were used to measure the CO<sub>2</sub> conversion ( $X_{CO_2}$ ), methane selectivity ( $S_{CH_4}$ ), the yield of methane ( $Y_{CH_4}$ ), and rate of methane formation, respectively.

$$X_{CO_2} = \frac{n(CH_4)_{out} + n(CO)_{out}}{n(CH_4)_{out} + n(CO_2)_{out} + n(CO)_{out}} \quad (3)$$

$$S_{CH_4} = \frac{n(CH_4)_{out}}{n(CH_4)_{out} + n(CO)_{out}} \quad (4)$$

$$Y_{CH_4} = X_{CO_2} \times S_{CH_4} \quad (5)$$

$$\text{Rate of } CH_4 \text{ formation (mmolm}^{-2}\text{/s}^{-1}) = \frac{n(CH_4)_{out}}{SA \times W.t} \quad (6)$$

where “n” indicates the moles of gases, including CH<sub>4</sub>, CO, and CO<sub>2</sub>; “SA” is the surface area (m<sup>2</sup>/g); “W” is the weight of the catalyst; and “t” is time.

## 3. Results and discussions

### 3.1. Morphological properties of the catalysts

Fig. 2 demonstrates the morphological properties of MOR and FS@SiO<sub>2</sub>-MOR. It is noteworthy that the morphology of MOR has changed entirely from the aggregated form (Fig. 2A) to produce sphere-shaped, well-formed nanoparticles of FS@SiO<sub>2</sub>-MOR (Fig. 2B), which showed cockscomb flower-like structure of uniform particle size in the range of 250–400 nm. These morphological properties were similar to KCC-1 reported by Polshettiwar (Polshettiwar et al., 2010). Furthermore, TEM analysis confirmed that a significant number of exterior fibers were produced on the core surface of the FS@SiO<sub>2</sub>-MOR (Fig. 2C and D) (the darker contrast area belonged to the mordenite zeolitic framework). It should be noted that these fibers are composed of silica species. A non-uniform and large inter-fiber distance can be seen, which may significantly improve the textural properties of the FS@SiO<sub>2</sub>-MOR.

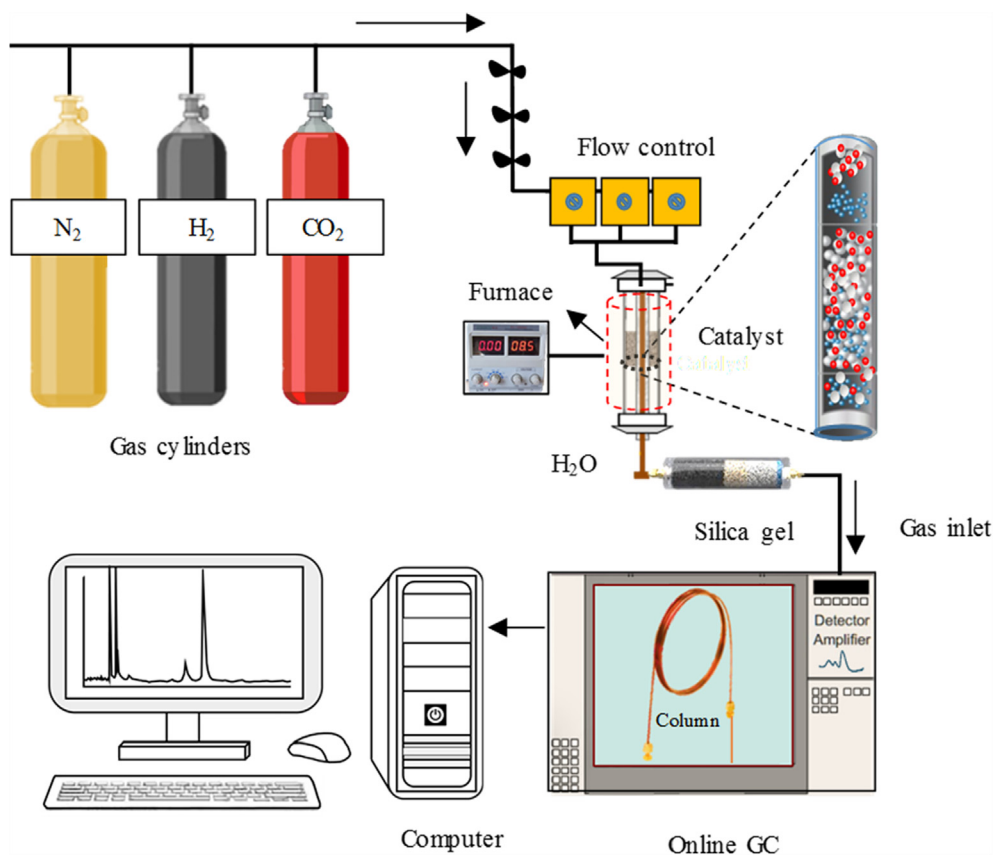


Fig. 1. Schematic experimental apparatus for catalytic CO<sub>2</sub> methanation.

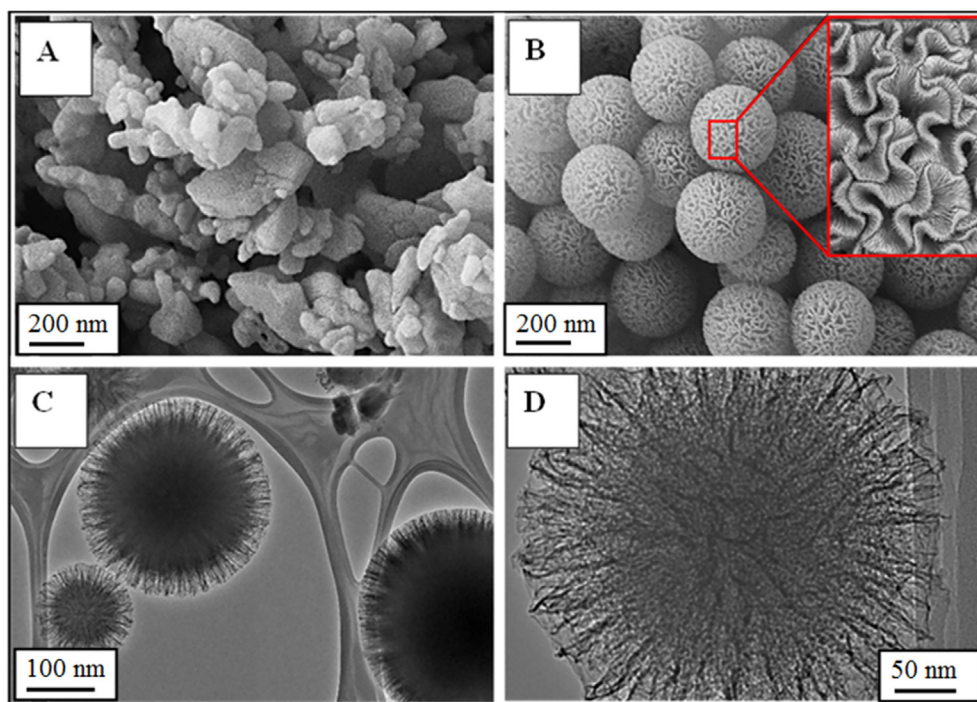


Fig. 2. FESEM images of (A) MOR, (B) FS@SiO<sub>2</sub>-MOR and TEM images of (C, D) FS@SiO<sub>2</sub>-MOR.

### 3.2. Textural properties

The surface properties of the catalysts were elucidated by  $N_2$  adsorption-desorption analysis, and the obtained results have been presented in Fig. 3. A reversible type IV isotherm was observed for the FS@SiO<sub>2</sub>-MOR (Fig. 3A), which is characteristic of mesoporous materials, while a reversible type I isotherm was noticed for the commercial MOR catalyst, which is characteristics of microporous materials (Thommes et al., 2015). It should be noted that the  $N_2$  adsorption happened at a lower relative pressure ( $P/P_0$ ) for both catalysts, which was due to the microporosity of the catalysts. The  $N_2$  adsorption at 0.45 and 0.93 relative pressures indicated the formation of new intra- and interparticle pores, respectively (Bernardoni and Fadeev, 2011). In a previous study, it was reported that these intra- and interparticle pores could improve the basicity of the catalysts (Aziz et al., 2014). Furthermore, the non-localized density functional theory (NLDFT) was used to measure the pore size distribution for both catalysts, shown in Fig. 3B. It is noteworthy that MOR showed a pore size distribution between 0 and 2 nm, which confirmed that commercial mordenite is a highly microporous material. In contrast, a new range of pore size distribution (2–6 nm) appeared for the FS@SiO<sub>2</sub>-MOR, which confirmed the formation of new mesopores due to the self-assembling of the cetyltrimethylammonium bromide (CTAB) (Teh et al., 2016).

Based on these textural changes, a remarkable enhancement was observed in the BET surface area (605 m<sup>2</sup>/g) and the pore volume (0.85 cm<sup>3</sup>/g) of the FS@SiO<sub>2</sub>-MOR, presented in Table 1. These textural observations strongly agree with the FESEM and TEM results in Fig. 2. Therefore, it is suggested that the surface modification of the FS@SiO<sub>2</sub>-MOR will improve accessibility and boost the adsorbance of H<sub>2</sub> and CO<sub>2</sub> molecules to enhance the catalytic activity for CO<sub>2</sub> methanation.

### 3.3. Structural properties

Fig. 4A shows the XRD patterns of MOR and FS@SiO<sub>2</sub>-MOR. It can be noticed that similar X-ray diffraction patterns have appeared for both catalysts. The diffraction peaks appeared at  $2\theta = 6.54^\circ, 8.76^\circ, 9.75^\circ, 13.54^\circ, 15.37^\circ, 19.71^\circ, 22.41^\circ, 25.76^\circ, 26.41^\circ, 27.75^\circ$  and  $31.07^\circ$ , with the corresponding planes (110),

(020), (200), (111), (310), (330), (150), (202), (350), (132) and (402), respectively. These observations were made according to the joint committee on powder diffraction standards: JCPDS 43-0171 (Narayanan et al., 2015; Xu et al., 2011). It is confirmed that both catalysts, MOR and FS@SiO<sub>2</sub>-MOR, are in the pure form of the orthorhombic phase of the mordenite structure, and the FS@SiO<sub>2</sub>-MOR was synthesized successfully, without any significant change. However, for the FS@SiO<sub>2</sub>-MOR, the peak intensity of different phases decreased significantly, indicating the loss of structural integrity during the modification process, which was due to the creation of new mesopores by amorphous silica, combined with the crystalline solid phases (the formation of new mesopores having been discussed in the previous section). It is therefore suggested that, after the growth of the silica fibers on MOR, the crystallinity of the FS@SiO<sub>2</sub>-MOR has been reduced significantly. Similar observations were found in previous studies (Izan et al., 2019; Firmansyah et al., 2016).

Fig. 4B displays the FTIR spectra for both MOR and FS@SiO<sub>2</sub>-MOR after evacuation for 1 h at 400 °C. It is noted that three leading bands have appeared at 3610, 3662, and 3740 cm<sup>-1</sup>, ascribed to hydroxyl groups such as the Si-OH-Al, Al-OH, and Si-OH, respectively (Yu et al., 2019). A sharp rise can be seen at 3740 cm<sup>-1</sup>, which is most probably due to the creation of new mesopores in the FS@SiO<sub>2</sub>-MOR. These observations are supported by the results of our previous  $N_2$  adsorption-desorption characterization, discussed in Section 3.2 (Fig. 3 and Table 1).

The FTIR technique is extensively employed to study the bending and stretching vibrations of different types of bonds existent in the framework of the catalysts. Fig. 4C presents the FTIR-KBr spectra for both MOR and FS@SiO<sub>2</sub>-MOR. It can be noted that similar FTIR bands of different absorption appeared at 3655 cm<sup>-1</sup>, 3420 cm<sup>-1</sup>, 1630 cm<sup>-1</sup>, 1220 cm<sup>-1</sup>, 1150–1050 cm<sup>-1</sup>, 960 cm<sup>-1</sup>, 810 cm<sup>-1</sup>, 709 cm<sup>-1</sup>, 590 cm<sup>-1</sup>, and 456 cm<sup>-1</sup>. The two bands at 3420 and 3655 cm<sup>-1</sup> are due to the stretching vibrations of the H<sub>2</sub>O molecules, which were absorbed on the catalyst's surface. The bands at 709, 811, 1090, and 1222 cm<sup>-1</sup> were the T-O bending absorption bands associated with the external and internal symmetric stretching, and asymmetric stretching vibrations, confirming the siliceous nature of both catalysts. Another spectral band was produced at 1630 cm<sup>-1</sup> because of the bending vibration of H<sub>2</sub>O molecules, which were absorbed in the zeolite framework

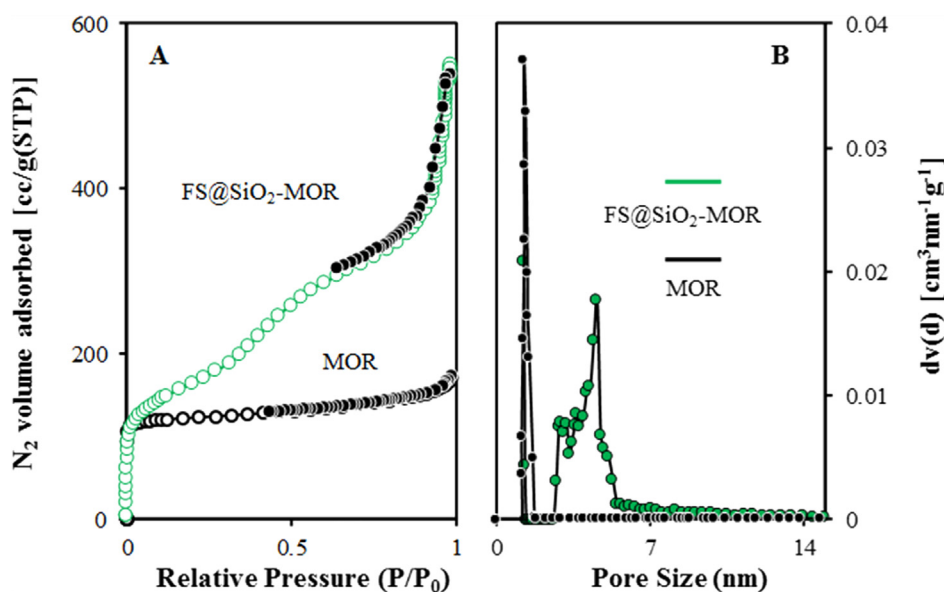


Fig. 3. (A)  $N_2$  adsorption (white symbols)-desorption (black symbols) isotherms and (B) NLDFT pore size distribution of MOR and FS@SiO<sub>2</sub>-MOR catalysts.

**Table 1**  
Physico-chemical properties of the catalysts.

| Catalysts                | Surface area <sup>a</sup><br>(m <sup>2</sup> /g) | Total pore volume <sup>a</sup><br>(cm <sup>3</sup> /g) | Mesopore volume <sup>a</sup><br>(cm <sup>3</sup> /g) | Micropore volume <sup>a</sup><br>(cm <sup>3</sup> /g) | Average pore size <sup>b</sup><br>(nm) | Type of isotherm <sup>a</sup> | Activation energy <sup>c</sup><br>(kJ/mol) E <sub>a</sub> |
|--------------------------|--------------------------------------------------|--------------------------------------------------------|------------------------------------------------------|-------------------------------------------------------|----------------------------------------|-------------------------------|-----------------------------------------------------------|
| FS@SiO <sub>2</sub> -MOR | 605                                              | 0.85                                                   | 0.78                                                 | 0.07                                                  | 4.2                                    | type I                        | 61.71                                                     |
| MOR                      | 326                                              | 0.26                                                   | 0.04                                                 | 0.22                                                  | 1.6                                    | type IV                       | 102.82                                                    |

<sup>a</sup> Determine from BET and non-local density functional theory (NLDFT).

<sup>b</sup> Total pore volume – micropore volume by t-plot method.

<sup>c</sup> E<sub>a</sub> values were determined using Arrhenius equation in the range of 300–500 °C.

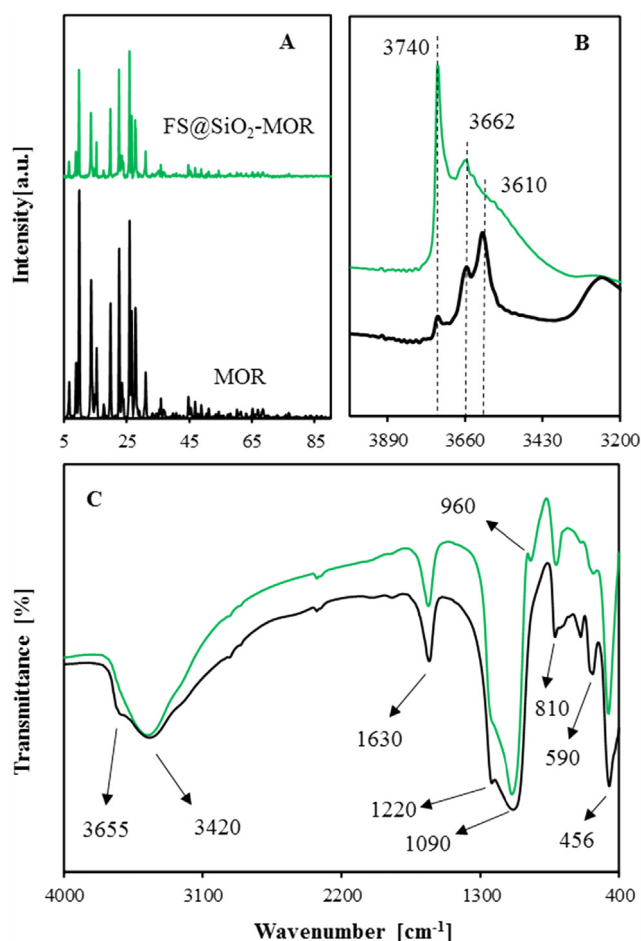


**Fig. 4.** (A) XRD diffractogram, (B) evacuated FTIR spectra, (C) FTIR-KBr spectra for MOR and FS@SiO<sub>2</sub>-MOR.

during the compaction of catalysts with the KBr particles. In addition, a weak band was observed at 960 cm<sup>-1</sup> only for the FS@SiO<sub>2</sub>-MOR, which might be assigned to bending vibrations of Si-OH. This might be due to the improved number of terminal silanol groups due to the formation of the silica fibers. The vibrational band produced at 590 cm<sup>-1</sup> is due to the tetrahedral structure of AlO<sub>4</sub> and SiO<sub>4</sub> and the double five-member ring in the catalysts (Prapainainar et al., 2019; Prapainainar et al., 2018). Based on the evaluations summarized above, it can be concluded that FS@SiO<sub>2</sub>-MOR was successfully prepared without any significant change, with the structure preserved after modification of the MOR.

### 3.4. Paramagnetic properties

ESR spectroscopy or electron paramagnetic resonance (EPR) is an advantageous method to elucidate the paramagnetic sites in the catalysts. It is also used to examine the unpaired electrons

and oxygen vacancies present in the materials. According to literature, g-values at 1.91, 1.95, and 1.99 during ESR signals indicate unpaired electrons and oxygen vacancies in the catalysts (Macdonald et al., 2010; Widmann et al., 2007; Zelenak et al., 2010). These g-values are the structural vibrations in the silica species (SiO<sub>2</sub>) due to the non-bridging oxygen hole centers (NBOHCs) or dangling bonds (E' centers), which may form on the conversion of the bulk SiO<sub>2</sub> into SiO<sub>x</sub> (x < 2). These sites may also act as magnetic sites or radical sites (Si•) with unpaired electrons (Jafarzadeh et al., 2012; Pan et al., 2014). In this study, ESR spectroscopy was conducted for both MOR and FS@SiO<sub>2</sub>-MOR, and results are presented in Fig. 5. It can be observed that FS@SiO<sub>2</sub>-MOR exhibited a high intensity of ESR signals at g = 1.91 and 1.99. The commercial MOR did not show significant ESR signals at g = 1.91 and 1.99. On the base of these observations, it is confirmed that FS@SiO<sub>2</sub>-MOR has high oxygen vacancies and unpaired electrons, which can be effective in improving the CO<sub>2</sub> methanation activity.

### 3.5. Basic properties

It is well known that the basic properties of the catalysts are very important for catalytic performance because basicity favors the CO<sub>2</sub> methanation reaction. Therefore, in this study, the basic properties of MOR and FS@SiO<sub>2</sub>-MOR were investigated by FTIR-pyrrole adsorption, as shown in Fig. 6. A broadening band at 3467 cm<sup>-1</sup> is due to hydrogen bonding between the H atom of pyrrole and the negatively charged O<sup>2-</sup> atom in the catalysts. Therefore, the 3467 cm<sup>-1</sup> band intensity specifies the strength of basicity in the catalysts (Forster et al., 1999; Huang et al., 1995). The FTIR spectra of pyrrole adsorption has also been shown between 1300 and 2100 cm<sup>-1</sup> (Fig. 6C). The adsorption at 1625, 1535, 1460, and 1423 cm<sup>-1</sup> indicates the aromatic C = C stretching vibration present in the pyrrole ring and O<sup>2-</sup> in the catalysts (Huang et al., 1995; Murphy et al., 1996). FS@SiO<sub>2</sub>-MOR showed higher peak intensity of all bands compared to MOR, which confirmed that the synthesized FS@SiO<sub>2</sub>-MOR has a higher level of basicity. It is suggested that basicity will be the critical factor to enhance the adsorption of acidic CO<sub>2</sub> molecules for improved CO<sub>2</sub> methanation. It was reported that the basicity and the oxygen vacancies in the catalyst have a close relationship (Climent et al., 2004; Drouilly et al., 2013). When an oxygen vacancy is produced in the catalyst, two unpaired electrons are left behind and trap in the catalyst, which could strengthen the Lewis basicity of the catalyst and enable it to interact more strongly with the CO<sub>2</sub> gas molecules. Consequently, the higher number of oxygen vacancies could endorse more Lewis basicity in the catalyst (Upham et al., 2015), which is crucial to promote and accelerate the chemical reaction between H<sub>2</sub> and CO<sub>2</sub> molecules to produce methane.

To further investigate the basic properties of the catalysts, the CO<sub>2</sub>-TPD was executed. The CO<sub>2</sub>-TPD profiles are shown in Fig. 7 for MOR and synthesized FS@SiO<sub>2</sub>-MOR. It can be seen that both catalysts exhibit a broad desorption peak at different temperatures, indicating that basic sites are present in the catalysts in a different form, including weak basic sites (100–230 °C), moderate

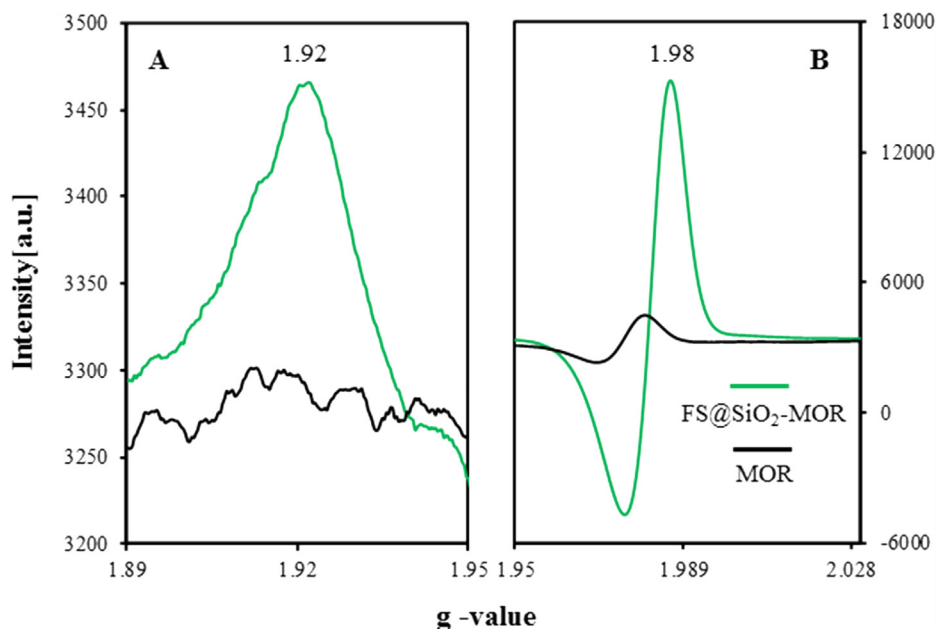


Fig. 5. ESR signals after evacuation at 400 °C for MOR and FS@SiO<sub>2</sub>-MOR.

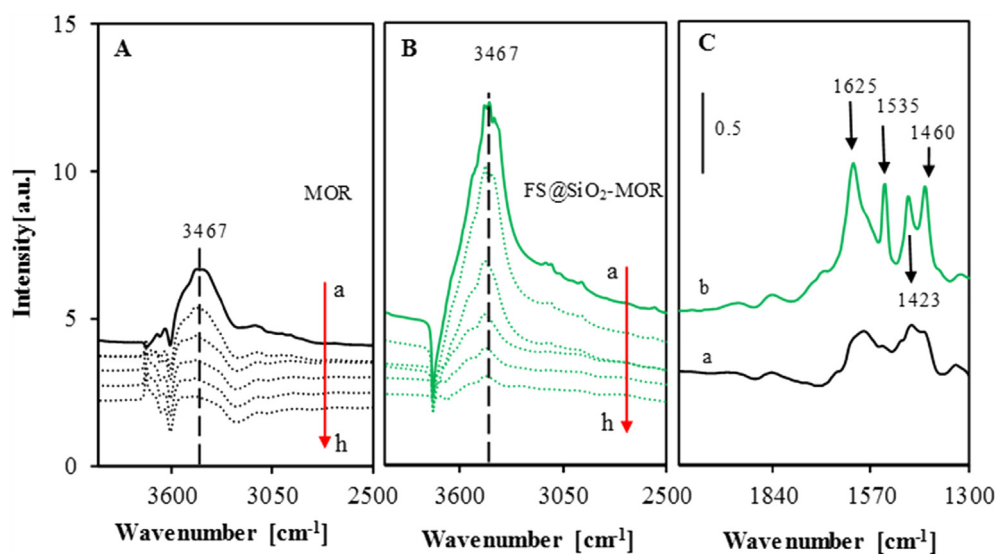


Fig. 6. FTIR spectra of pyrrole adsorbed on (A) MOR and (B) FS@SiO<sub>2</sub>-MOR at (a) room temperature and outgassing (dotted lines) at (b) room temperature (c) 50 °C (d) 100 °C (e) 150 °C and (h) 200 °C. (C) FTIR by pyrrole adsorption in the range of 1300–2100 cm<sup>-1</sup> on (a) MOR (b) FS@SiO<sub>2</sub>-MOR catalysts.

basic sites (230–500 °C) and strong (above 500 °C) basic sites (Prymak et al., 2015). It is obvious that the prepared FS@SiO<sub>2</sub>-MOR catalyst exhibited the high CO<sub>2</sub>-TPD signals, which confirmed a higher concentration of the basic sites compared to MOR.

### 3.6. Catalytic performance of CO<sub>2</sub> methanation

FS@SiO<sub>2</sub>-MOR and MOR were used in the CO<sub>2</sub> methanation reaction. Fig. 8 illustrates the catalytic performance in terms of CH<sub>4</sub> selectivity, CO<sub>2</sub> conversion, and CH<sub>4</sub> yield in the range of 250 to 500 °C. The corresponding thermodynamic equilibrium (theoretical) values were also calculated and have been included in Fig. 8 (A, and C) for comparison. It can be observed that, for both MOR and FS@SiO<sub>2</sub>-MOR, the CO<sub>2</sub> methanation activity was much lower than that allowed by thermodynamics at reaction temperatures below 400 °C. This could be because the activation energy is

not enough for the CO<sub>2</sub> methanation reaction at the lower temperatures. However, with increasing reaction temperature, the catalytic performance was improved significantly, reaching its highest value when the temperature was set at 500 °C. It should be noted that, above 450 °C, the CO<sub>2</sub> methanation reaction has started to attain thermodynamic equilibrium, and the CO<sub>2</sub> methanation activity became slow. This might be due to the CO by-product, which is produced by the reversed water gas shift reaction: CO<sub>2</sub> + H<sub>2</sub> → H<sub>2</sub>O + CO. Meanwhile, unreacted CO<sub>2</sub> and H<sub>2</sub> also increase at an elevated temperature (above 450 °C) (Gao et al., 2012). It is noteworthy that MOR showed a CH<sub>4</sub> selectivity of 37% (Fig. 8A), CO<sub>2</sub> conversion of 53% (Fig. 8B), and CH<sub>4</sub> yield of 24% (Fig. 8C), with the rate of CH<sub>4</sub> formation of  $0.44 \times 10^{-4}$  mmol m<sup>-2</sup>/s<sup>-1</sup> (Fig. 8D), while FS@SiO<sub>2</sub>-MOR demonstrated a higher CH<sub>4</sub> selectivity of 68%, CO<sub>2</sub> conversion of 65% and CH<sub>4</sub> yield of 43% with the rate of CH<sub>4</sub> formation of  $0.76 \times 10^{-4}$  mmol m<sup>-2</sup>/s<sup>-1</sup> at the same

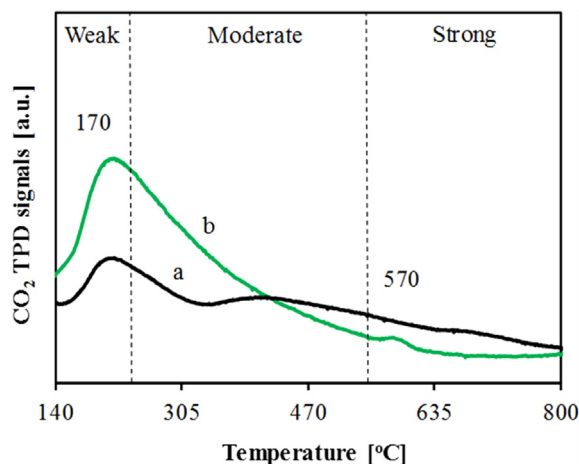


Fig. 7. CO<sub>2</sub>-TPD observations for (a) commercial MOR and (b) FS@SiO<sub>2</sub>-MOR catalysts.

temperature (500 °C). It is interesting to note that these experimental values are close to the theoretical values of CO<sub>2</sub> methanation activity at high temperatures. The theoretical values of CH<sub>4</sub> selectivity, CO<sub>2</sub> conversion, and CH<sub>4</sub> yield were 92%, 71%, and 64%, respectively, at a temperature of 500 °C. The Arrhenius plots and activation energy values for both MOR and FS@SiO<sub>2</sub>-MOR were also calculated and are shown in Fig. 9 and Table 1. It can be seen that the activation energy of FS@SiO<sub>2</sub>-MOR (61.71 kJ/mol) was lower than MOR (102.82 kJ/mol), which confirmed that FS@SiO<sub>2</sub>-MOR is a more active and efficient catalyst for the CO<sub>2</sub> methanation reaction compared to MOR.

Typically, metal promoted catalysts are used in CO<sub>2</sub>/CO methanation reactions, where metals behave as an active phase or active site for CO<sub>2</sub> and H<sub>2</sub> molecules. In this study, the oxygen vacancies and basicity of FS@SiO<sub>2</sub>-MOR played a crucial role in the activation of CO<sub>2</sub> and H<sub>2</sub> molecules during methane formation. According to previous studies, different defects can dissociate molecular hydrogen into atomic hydrogen, such as neutral oxygen vacancies ( $\equiv\text{Si}$ ),

divalent ( $\text{Si} = \text{Si}$ ), the E' centers ( $\equiv\text{Si}^*$ ) or Si atoms with  $\text{sp}^3$  dangling bonds, and the non-bridging oxygen centers or NBOs ( $\equiv\text{Si}-\text{O}^*$ ). Based on the literature, silica can dissociate hydrogen into atomic hydrogen (Vitiello et al., 2000). The high performance of FS@SiO<sub>2</sub>-MOR is also due to surface area and high basicity, as discussed in previous sections. Aziz et al. also conducted CO<sub>2</sub> methanation and compared different types of Ni-promoted supports towards CO<sub>2</sub> methanation activity, such as MSN, MCM-41, Y zeolite, SiO<sub>2</sub>, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. They found that Ni-MSN exhibited superior activity due to higher basicity, oxygen vacancies and high surface area (Aziz et al., 2014). In another study, Jia et al. performed CO<sub>2</sub> methanation over Ni/ZrO<sub>2</sub> and reported that CO<sub>2</sub> methanation activity was increased due to the high amount of oxygen vacancies present in the catalyst (Jia et al., 2019). Italiano et al. investigated different supports (CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub>) for CO<sub>2</sub> methanation. They found that Y<sub>2</sub>O<sub>3</sub> expressed a higher CO<sub>2</sub> conversion (69.8%) than CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (Italiano et al., 2020). Hamid et al. synthesized fibrous KCC-1 and applied CO<sub>2</sub> methanation. They found a CO<sub>2</sub> conversion of 48.7% and a CH<sub>4</sub> yield of 38.9% at 500 °C (Hamid et al., 2017). Chang et al. conducted hydrogenation of CO<sub>2</sub> over nickel-supported catalysts (Ni/MCM-41). They reported 35.8% of CO<sub>2</sub> conversion and 11.1% CH<sub>4</sub> yield (Chang et al., 2001). In the light of the reports mentioned above, it can be concluded that the synergistic effect of basic sites and oxygen vacancies in FS@SiO<sub>2</sub>-MOR assisted the activation and dissociation process for CO<sub>2</sub> and H<sub>2</sub>, enhancing the CO<sub>2</sub> methanation activity.

### 3.7. Catalytic stability

For both MOR and FS@SiO<sub>2</sub>-MOR catalysts, the thermal stability was examined for 50 h on stream at 500 °C, the optimum temperature for maximum catalytic activity of CO<sub>2</sub> methanation. As shown in Fig. 10A, the MOR catalyst displayed 36% CH<sub>4</sub> selectivity, which showed a significant decrease after 28 h of reaction, demonstrating that the MOR catalyst deactivated dramatically. The FS@SiO<sub>2</sub>-MOR catalyst exhibited unchanged catalytic activity (CH<sub>4</sub> selectivity 68%) during the reaction for 50 h; thus, these observations indicate that the FS@SiO<sub>2</sub>-MOR catalyst improved

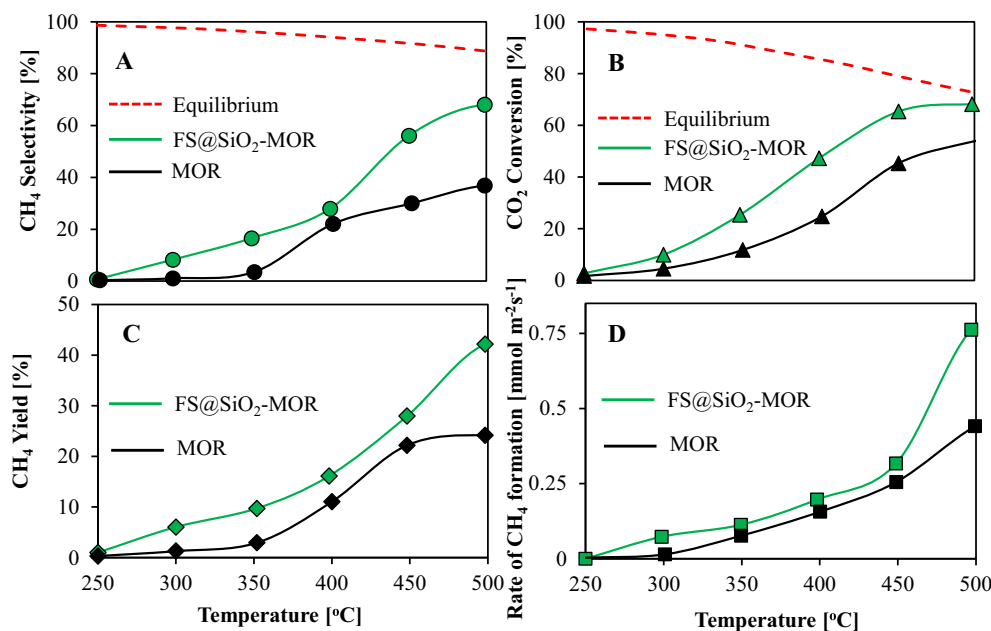


Fig. 8. (A) Selectivity of CH<sub>4</sub>, (B) CO<sub>2</sub> conversion, (C) CH<sub>4</sub> yield, and (D) rate of formation of CH<sub>4</sub>. Thermodynamic equilibrium (red colour) calculated using by HSC Chemistry 6.0 software.

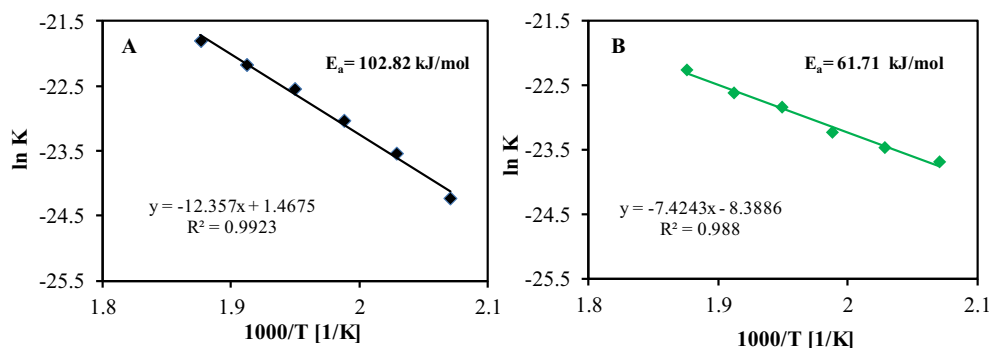


Fig. 9. Arrhenius plots for (A) MOR and (B) FS@SiO<sub>2</sub>-MOR catalysts.

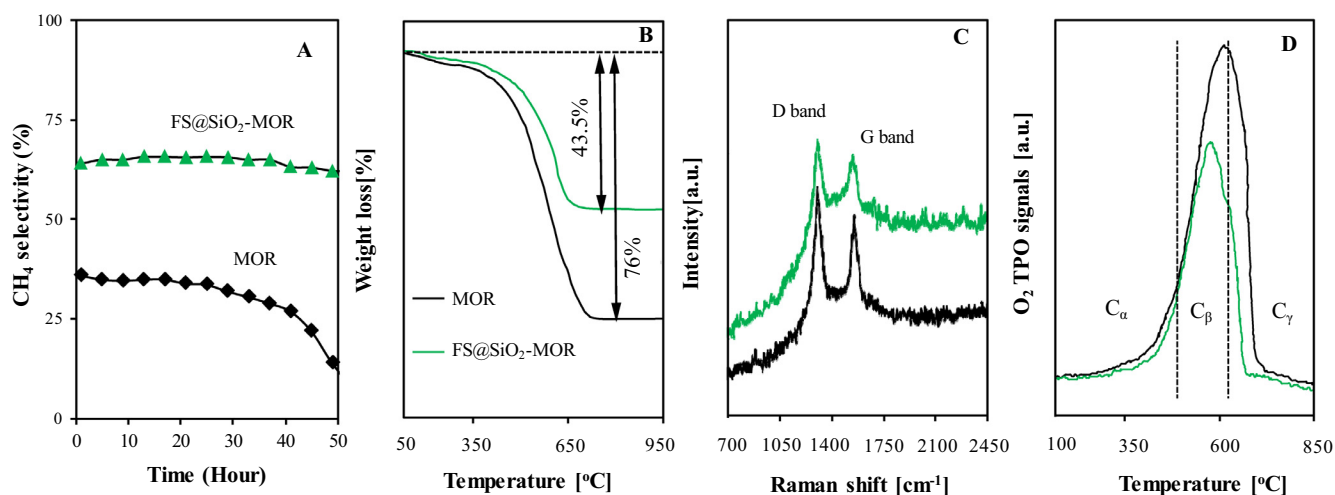


Fig. 10. (A) Thermal stability, (B) TGA analysis, (C) Raman spectra, and (D) TPO analysis of the spent MOR and FS@SiO<sub>2</sub>-MOR catalysts after long-term thermal stability of 50 h.

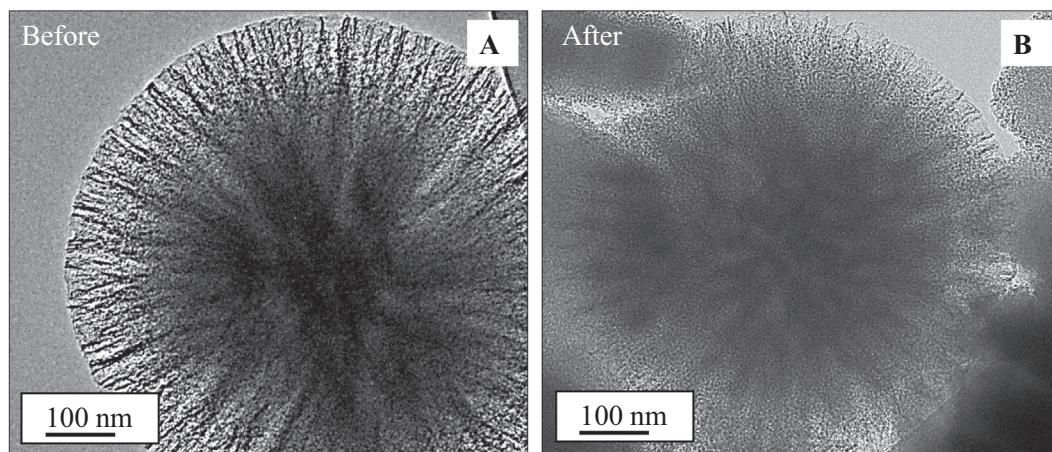


Fig. 11. TEM analysis of (A) fresh FS@SiO<sub>2</sub>-MOR, (B) spent FS@SiO<sub>2</sub>-MOR after long-term thermal stability test of 50 h.

the catalytic stability for the CO<sub>2</sub> methanation reaction. The possible reason for the deactivation of MOR is coke deposition, which could cover the active sites and block the pores during catalytic performance. Thus, it is concluded that the unique fibrous morphology of the FS@SiO<sub>2</sub>-MOR catalyst was able to retard coke deposition and deactivation by suppressing undesired side reactions during the CO<sub>2</sub> methanation reaction.

### 3.8. Analysis of spent catalysts

Thermal gravimetric analysis (TGA) was conducted to examine the coke deposition on both spent MOR and FS@SiO<sub>2</sub>-MOR catalysts after the 50 h thermal stability test, and the results have been displayed in Fig. 10B. It can be seen that both MOR (76% weight loss) and FS@SiO<sub>2</sub>-MOR (43.5% weight loss) displayed weight loss

upon increasing the temperature. However, synthesized FS@SiO<sub>2</sub>-MOR showed less weight loss than MOR, which indicates that less carbon deposition was produced on FS@SiO<sub>2</sub>-MOR during CO<sub>2</sub> methanation activity.

The composition and structure of the coke deposition produced during a chemical reaction can also be investigated by Raman spectroscopy (Vogelaar et al., 2007). Therefore, Raman spectroscopy was performed on both spent MOR and FS@SiO<sub>2</sub>-MOR catalysts after the 50 h thermal stability test, and the results have been displayed in Fig. 10C. It can be observed that both catalysts showed two leading bands at 1350 and 1585 cm<sup>-1</sup>, which are called the D-band (disorder-induced band) and G-band (graphite-like band),

respectively. The D-band generally appears due to the vibration of an amorphous carbon network with dangling bonds. In contrast, the G-band is produced due to stretching vibrations of carbons atoms bonded through sp<sup>2</sup> hybridization, also called graphitic carbons. The simultaneous existence of D and G bands illustrates that both MOR and FS@SiO<sub>2</sub>-MOR showed the amorphous and graphite carbon during the reaction. However, FS@SiO<sub>2</sub>-MOR showed less intensity of these two bands compared to MOR. In addition, the degree of crystallization of graphitic carbon can be calculated by the ratio of these two bands (IG/ID) (Pang et al., 2010). A higher ratio of IG/ID reveals a higher amount of graphitic carbon than amorphous carbon. It is well known that graphitic carbon is considered a more stable form of carbon deposition, which could deactivate the catalysts. It is evident that MOR showed an IG/ID ratio of 0.92, while FS@SiO<sub>2</sub>-MOR exhibited a 0.59 ratio, which confirmed that the synthesized FS@SiO<sub>2</sub>-MOR exhibited less graphitic carbon than MOR due to its unique fibrous morphology. This is highly consistent with the thermal stability test (Fig. 10A) and suggests that FS@SiO<sub>2</sub>-MOR showed more thermal stability due to less graphitic carbon than MOR.

The temperature-programmed oxidation (TPO) study was executed on both MOR and FS@SiO<sub>2</sub>-MOR after the stability test to further examine the quantity and characteristics of carbon deposition. The TPO profiles have been shown in Fig. 10D over the 100–850 cm<sup>-1</sup> region. It can be observed that a significant amount of TPO signals appeared for both MOR and FS@SiO<sub>2</sub>-MOR samples. According to literature, the TPO signal area can be divided into three regions based on temperatures such as C<sub>α</sub> (350–450 °C), C<sub>β</sub> (450–600 °C), and C<sub>γ</sub> (600–750 °C). These regions indicate the amorphous carbon, filaments carbon, and graphite carbon, respectively, which are called D-band (disorder-induced band) and G-band (graphite-like band), respectively. These carbon species are arranged in the following decreasing order: C<sub>α</sub> > C<sub>β</sub> > C<sub>γ</sub>, which is

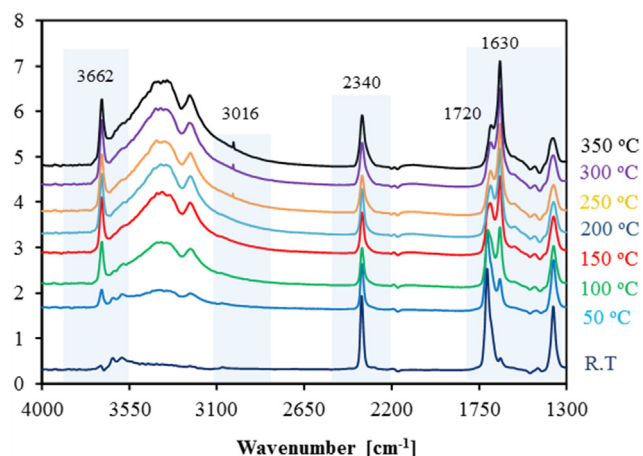


Fig. 12. In-situ FTIR spectra after adsorption of H<sub>2</sub> + CO<sub>2</sub> on FS@SiO<sub>2</sub>-MOR in the temperature range 50–350 °C.

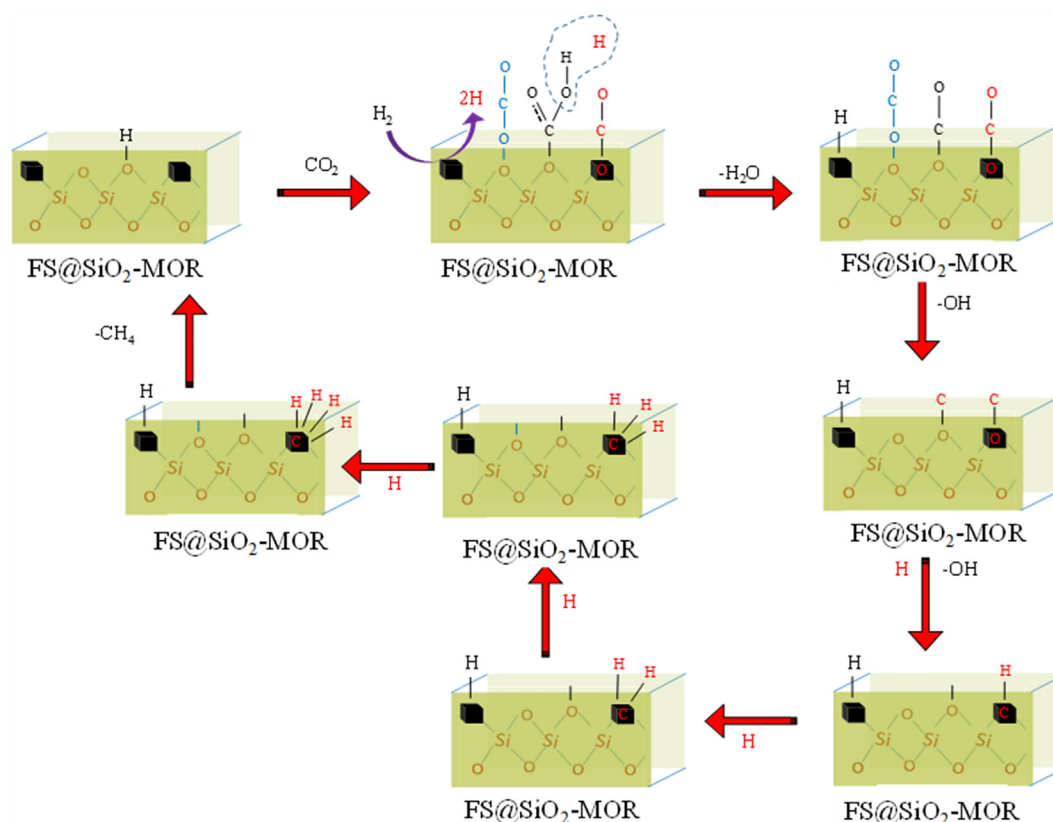


Fig. 13. Possible reaction mechanism of formation methane during catalytic CO<sub>2</sub> methanation over FS@SiO<sub>2</sub>-MOR, where " " presents oxygen vacancy.

based on the activity with oxygen (Liang et al., 2019). It can be observed that FS@SiO<sub>2</sub>-MOR exhibited a weaker TPO peak area than MOR, which indicates that FS@SiO<sub>2</sub>-MOR has the less amount of carbon deposition. It should be noted that C<sub>α</sub> is still reactive in the high-temperature reaction and can participate in the CO<sub>2</sub> methanation reaction because it is easy to eliminate. Nevertheless, C<sub>γ</sub> species are thermally stable and very difficult to remove at high temperatures; thus, this species could cover the active sites and pores to decrease the catalyst's surface reaction. These results are consistent with TGA and Raman characterization results. To study the morphological properties of spent FS@SiO<sub>2</sub>-MOR, TEM analysis has been performed and shown in Fig. 11. It is clear that there was no morphological change in FS@SiO<sub>2</sub>-MOR after catalytic activity, and it maintained its fibrosity after the 50 h stability test of the CO<sub>2</sub> methanation reaction Fig. 11B. Based on the above results, it is concluded that FS@SiO<sub>2</sub>-MOR can resist coke deposition and maintain stability longer than MOR due to its unique fibrous morphology.

### 3.9. Reaction mechanism study of CO<sub>2</sub> methanation

The reaction pathways for the CO<sub>2</sub> methanation reaction have been a debatable subject in the field of heterogeneous catalysis. To investigate the reaction mechanism of CO<sub>2</sub> methanation, we examined the intermediate species produced on the surface of FS@SiO<sub>2</sub>-MOR during the CO<sub>2</sub> methanation reaction. An in-situ FTIR spectroscopy was executed in the range of 4000–1300 cm<sup>-1</sup>, and the recorded spectra have been presented in Fig. 12. At room temperature, different bands appeared at 1357 cm<sup>-1</sup> and 1442 cm<sup>-1</sup>, representing the formate and monodentate carbonates, respectively (Wang et al., 2016), while the bands at 1630 cm<sup>-1</sup> and 1720 cm<sup>-1</sup> represented the symmetric O=C=O stretching modes of carbonyls, and the band at 2340 cm<sup>-1</sup> is attributed to linear CO<sub>2</sub> (Aziz et al., 2014). We have noticed that surface species have a strong correlation with temperature, as it can be seen that 1357, 1720, and 2340 cm<sup>-1</sup> bands significantly decreased on increasing the temperature, while the band at 1630 cm<sup>-1</sup> started to grow at higher temperatures, suggesting that these intermediate surface species played a critical role in the production of methane. It should be noted that a new band appeared at 3016 cm<sup>-1</sup> when the temperature was 250 °C, attributed to methane in the gas phase (Hussain et al., 2019), which improved as the temperature increased. These observations are in accordance with experimental CO<sub>2</sub> methanation results (Fig. 8). Furthermore, the FTIR spectra in the range of 3100–3550 cm<sup>-1</sup> presented stretching vibrations of water molecules which have adsorbed physically and chemically on the catalyst's surface, as it is clear that water is the main component produced during CO<sub>2</sub> methanation activity (Eq. (2)). The bands that appeared above 3600 cm<sup>-1</sup> were ascribed to surface OH groups (Radtke et al., 2016). It should be noted that no significant CO band was detected during in-situ FTIR observations. Therefore, it can be concluded that an associative mechanism was involved by the associative adsorption of CO<sub>2</sub> and H<sub>2</sub> via oxygenate species, such as carbonyls and linear CO<sub>2</sub><sup>\*</sup>, which were hydrogenated to form methane in different steps, as shown in Fig. 13. Thus, based on in-situ FTIR observations, it is concluded that an associative mechanism was followed during the CO<sub>2</sub> methanation reaction.

## 4. Conclusion

A fibrous silica-mordenite (FS@SiO<sub>2</sub>-MOR) cockscomb shaped catalyst was successfully prepared through the microemulsion process. The prepared FS@SiO<sub>2</sub>-MOR was characterized and compared with commercial mordenite (MOR) with regard to CO<sub>2</sub>

methanation activity. It was found that FS@SiO<sub>2</sub>-MOR illustrated superior activity (CO<sub>2</sub> conversion 65% and CH<sub>4</sub> selectivity 68%) with higher thermal stability (50 h) than MOR. This was due to the innovative fibrous morphology of FS@SiO<sub>2</sub>-MOR, which provided a high surface area and a large number of oxygen vacancies and basic sites to adsorb more CO<sub>2</sub> and H<sub>2</sub> molecules. In addition, the oxygen vacancies played a crucial role in conducting the activation of CO<sub>2</sub> and H<sub>2</sub> during CO<sub>2</sub> methanation activity. FS@SiO<sub>2</sub>-MOR retarded coke deposition by suppressing unwanted coke-producing reactions during CO<sub>2</sub> methanation activity. According to in-situ FTIR observations, it is concluded that the carbonyls and linear CO<sub>2</sub><sup>\*</sup> were important intermediates in methane formation during CO<sub>2</sub> methanation activity. Thus, in the present study, an associative mechanism was followed during the CO<sub>2</sub> methanation reaction. These promising results illustrate the potential of FS@SiO<sub>2</sub>-MOR as an active and efficient catalyst for the CO<sub>2</sub> methanation reaction.

### CRedit authorship contribution statement

**I. Hussain:** Conceptualization, Methodology, Investigation, Resources, Formal analysis, Visualization, Writing - original draft. **A.A. Jalil:** Writing - review & editing, Supervision, Project administration, Funding acquisition. **N.S. Hassan:** Validation, Formal analysis, Visualization. **H.U. Hambali:** Writing - review & editing. **N.W. C. Jusoh:** Writing - review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### References

- Aziz, M.A.A., Jalil, A.A., Triwahyono, S., Sidik, S.M., 2014. Methanation of carbon dioxide on metal-promoted mesostructured silica nanoparticles. *Appl. Catal. A: Gen.* 486, 115–122. <https://doi.org/10.1016/j.apcata.2014.08.022>.
- Aziz, M.A.A., Jalil, A.A., Triwahyono, S., Mukti, R.R., Taufiq-Yap, Y.H., Sazegar, M.R., 2014. Highly active Ni-promoted mesostructured silica nanoparticles for CO<sub>2</sub> methanation. *Appl. Catal. B* 147, 359–368. <https://doi.org/10.1016/j.apcatb.2013.09.015>.
- Azzolina-Jury, Federico, Bento, Diogo, Henriques, Carlos, Thibault-Starzyk, Frédéric, 2017. Chemical engineering aspects of plasma-assisted CO<sub>2</sub> hydrogenation over nickel zeolites under partial vacuum. *J. CO<sub>2</sub> Utilization* 22, 97–109. <https://doi.org/10.1016/j.jcou.2017.09.017>.
- Bai, S., Shao, Q., Wang, P., Dai, Q., Wang, X., Huang, X., 2017. Highly active and selective hydrogenation of CO<sub>2</sub> to ethanol by ordered Pd-Cu nanoparticles. *J. Am. Chem. Soc.* 139 (20), 6827–6830. <https://doi.org/10.1021/jacs.7b03101>.
- Bernardoni, F., Fadeev, A.Y., 2011. Adsorption and wetting characterization of hydrophobic SBA-15 silicas. *J. Colloid Interface Sci.* 356 (2), 690–698. <https://doi.org/10.1016/j.jcis.2011.01.033>.
- Brooks, K.P., Hu, J., Zhu, H., Kee, R.J., 2007. Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors. *Chem. Eng. Sci.* 62 (4), 1161–1170. <https://doi.org/10.1016/j.ces.2006.11.020>.
- Cardenas-Arenas, A., Quindimil, A., Davo-Quinonero, A., Bailon-Garcia, E., Lozano-Castello, D., De-La-Torre, U., et al., 2019. Isotopic and in situ DRIFTS study of the CO<sub>2</sub> methanation mechanism using Ni/CeO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. *Appl. Catal. B*. <https://doi.org/10.1016/j.apcatb.2019.118538>.
- Chang, F.W., Tsay, M.T., Liang, S.P., 2001. Hydrogenation of CO<sub>2</sub> over nickel catalysts supported on rice husk ash prepared by ion exchange. *Appl. Catal. A: Gen.* 209 (1–2), 217–227. [https://doi.org/10.1016/S0926-860X\(00\)00772-9](https://doi.org/10.1016/S0926-860X(00)00772-9).
- Climent, M.J., Corma, A., Iborra, S., Epping, K., Velty, A., 2004. Increasing the basicity and catalytic activity of hydrotalcites by different synthesis procedures. *J. Catal.* 225 (2), 316–326. <https://doi.org/10.1016/j.jcat.2004.04.027>.
- Drouilly, C., Krafft, J.M., Averseng, F., Lauron-Pernot, H., Bazer-Bachi, D., Chizallet, C., Lecomte, V., Costentin, G., 2013. Role of oxygen vacancies in the basicity of ZnO:

- From the model methylbutynol conversion to the ethanol transformation application. *Appl. Catal. A Gen.* 453, 121–129. <https://doi.org/10.1016/j.apcata.2012.11.045>.
- Fatah, N.A.A., Jalil, A.A., Rahman, A.F.A., Hambali, H.U., Hussain, I., 2019. CO<sub>2</sub> methanation over mesoporous silica based catalyst: a comprehensive study. *J. Energy Saf. Technol.*, 49–53 <https://doi.org/10.1113/jest.v2n2.51>.
- Fatah, N.A.A., Jalil, A.A., Triwahyono, S., Yusof, N., Mamat, C.R., Izan, S.M., Hamid, M.Y.S., Hussain, I., Adnan, R.H., Abdullah, T.A.T., Nabgan, W., 2020. Favored hydrogenation of linear carbon monoxide over cobalt loaded on fibrous silica KCC-1. *Int. J. Hydrogen Energy* 45 (16), 9522–9534. <https://doi.org/10.1016/j.ijhydene.2020.01.144>.
- Feng, Y., Yang, W., Chen, S., Chu, W., 2014. Cerium promoted nano nickel catalysts Ni-Ce/CNTs and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> for CO<sub>2</sub> methanation. *Integrated Ferroelectrics* 151 (1), 116–125. <https://doi.org/10.1080/10584587.2014.901141>.
- Firmansyah, M.L., Jalil, A.A., Triwahyono, S., Hamdan, H., Salleh, M.M., Ahmad, W.F.W., Kadja, G.T.M., 2016. Synthesis and characterization of fibrous silica ZSM-5 for cumene hydrocracking. *Catal. Sci. Technol.* 6 (13), 5178–5182. <https://doi.org/10.1039/C6CY00106H>.
- Forster, H., Fuess, H., Geidel, E., Hunger, B., Jobic, H., Kirschhock, C., Klepel, O., Krause, K., 1999. Adsorption of pyrrole derivatives in alkali metal cation-exchanged faujasites: comparative studies by surface vibrational techniques, X-ray diffraction and temperature-programmed desorption augmented with theoretical studies Part I. Pyrrole as probe molecule. *Phys. Chem. Chem. Phys.* 1 (4), 593–603. <https://doi.org/10.1039/A807296E>.
- Frontera, P., Macario, A., Ferraro, M., Antonucci, P., 2017. Supported catalysts for CO<sub>2</sub> methanation: a review. *Catalysts* 7 (2), 59. <https://doi.org/10.3390/catal7020059>.
- Gao, J., Wang, Y., Ping, Y., Hu, D., Xu, G., Gu, F., Su, F., 2012. A thermodynamic analysis of methanation reactions of carbon oxides for the production of synthetic natural gas. *RSC Adv.* 2 (6), 2358–2368. <https://doi.org/10.1039/C2RA00632D>.
- Ghani, N.N.M., Jalil, A.A., Triwahyono, S., Aziz, M.A.A., Rahman, A.F.A., Hamid, M.Y.S., Izan, S.M., Nawawi, M.G.M., 2019. Tailored mesoporosity and acidity of shape-selective fibrous silica beta zeolite for enhanced toluene co-reaction with methanol. *Chem. Eng. Sci.* 193, 217–229. <https://doi.org/10.1016/j.ces.2018.09.009>.
- Hambali, H.U., Jalil, A.A., Abdurashied, A.A., Siang, T.J., Fatah, N.A.A., Rahman, A.F.A., Aziz, M.A.H., Hussain, I., 2020. Effect of transition metals (Mo, Mn and Co) on mesoporous ZSM-5 catalyst activity in carbon dioxide reforming of methane. *Mater. Sci. Eng.* 808, <https://doi.org/10.1088/1757-899X/808/1/012005> 012005.
- Hamid, M.Y.S., Firmansyah, M.L., Triwahyono, S., Jalil, A.A., Mukti, R.R., Febriyanti, E., Suendo, V., Setiabudi, H.D., Mohamed, M., Nabgan, W., 2017. Oxygen vacancy-rich mesoporous silica KCC-1 for CO<sub>2</sub> methanation. *Appl. Catal. A: Gen.* 532, 86–94. <https://doi.org/10.1016/j.apcata.2016.12.023>.
- Hamid, M.Y.S., Jalil, A.A., Rahman, A.F.A., Abdullah, T.A.T., 2019. Enhanced reactive CO<sub>2</sub> species formation via V<sub>2</sub>O<sub>5</sub>-promoted Ni/KCC-1 for low temperature activation of CO<sub>2</sub> methanation. *React. Chem. Eng.* 4 (6), 1126–1135. <https://doi.org/10.1039/C8RE00312B>.
- Huang, M., Kaliaguine, S., Auroux, A., 1995. Lewis basic and Lewis acidic sites in zeolites. *Stud. Surf. Sci. Catal.* 97, 311–318. [https://doi.org/10.1016/S0167-2991\(06\)81903-8](https://doi.org/10.1016/S0167-2991(06)81903-8).
- Hussain, I., Jalil, A.A., Fatah, N.A.A., Ibrahim, M., Azami, M.S., Fadlun, W., Aziz, H., Hambali, H.U., 2020. A viable system for carbon dioxide (CO<sub>2</sub>) methanation over fibrous silica ZSM-5 for substitute natural gas (SNG). *Mater. Sci. Eng.* (808), 012037. <https://doi.org/10.1088/1757-899X/808/1/012037>.
- Hussain, I., Jalil, A.A., Mamat, C.R., Siang, T.J., Rahman, A.F.A., Azami, M.S., Adnan, R.H., 2019. New insights on the effect of the H<sub>2</sub>/CO ratio for enhancement of CO methanation over metal-free fibrous silica ZSM-5: Thermodynamic and mechanistic studies. *Energy Convers. Manag.* 199, <https://doi.org/10.1016/j.enconman.2019.112056>.
- Hussain, I., Jalil, A.A., Mamat, C.R., Siang, T.J., Azami, M.S., Hambali, H.U., 2019. Role of Promoters in Hoisting the Catalytic Performance for Enhanced CO Methanation. *J. Energy Saf. Technol.*, 15–20 <https://doi.org/10.1113/jest.v2n1.38>.
- Hussain, I., Jalil, A.A., Fatah, N.A.A., Hamid, M.Y.S., Ibrahim, M., Aziz, M.A.A., Setiabudi, H.D., 2020. A highly competitive system for CO methanation over an active metal-free fibrous silica mordenite via in-situ ESR and FTIR studies. *Energy Convers. Manag.* 211, <https://doi.org/10.1016/j.enconman.2020.112754> 112754.
- Hussain, I., Jalil, A.A., Fatah, N.A.A., Izan, S.M., Azami, M.S., 2020. Cockscomb-like fibrous silica beta zeolite (FSBEA) as a new engineered catalyst for enhanced CO methanation. *Mater. Sci. Eng.* 736, (4). <https://doi.org/10.1088/1757-899X/736/4/042012> 042012.
- Italiano, C., Ilorca, J., Pino, L., Ferraro, M., Antonucci, V., Vita, A., 2020. CO and CO<sub>2</sub> methanation over Ni catalysts supported on CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> oxides. *Appl. Catal. B* 264, <https://doi.org/10.1016/j.apcatb.2019.118494> 118494.
- Izan, S.M., Triwahyono, S., Jalil, A.A., Majid, Z.A., Fatah, N.A.A., Hamid, M.Y.S., Ibrahim, M., 2019. Additional Lewis acid sites of protonated fibrous silica@BEA zeolite (HSi@BEA) improving the generation of protonic acid sites in the isomerization of C<sub>6</sub> alkane and cycloalkanes. *Appl. Catal. A: Gen.* 570, 228–237. <https://doi.org/10.1016/j.apcata.2018.11.028>.
- Jafarzadeh, M., Adnan, R., Mazlan, M.K.N., 2012. Thermal stability and optical property of ormocers (organically modified ceramics) nanoparticles produced from copolymerization between amino-silanes and tetraethoxysilane. *J. Non-cryst. Solids* 358 (22), 2981–2987. <https://doi.org/10.1016/j.jnoncrsol.2012.07.028>.
- Jia, X., Zhang, X., Rui, N., Hu, X., Liu, C.J., 2019. Structural effect of Ni/ZrO<sub>2</sub> catalyst on CO<sub>2</sub> methanation with enhanced activity. *Appl. Catal. B* 244, 159–169. <https://doi.org/10.1016/j.apcatb.2018.11.024>.
- Lars, K., Jorg, T., 2015. Predicting optimal temperature profiles in single-stage fixed-bed reactors for CO<sub>2</sub>-methanation. *Chem. Eng. Sci.* 132, 59–71. <https://doi.org/10.1016/j.ces.2015.03.068>.
- Lee, S.M., Lee, Y.H., Moon, D.H., Ahn, J.Y., Nguyen, D.D., Chang, S.W., Kim, S.S., 2019. Reaction Mechanism and Catalytic Impact of Ni/CeO<sub>2-x</sub> Catalyst for Low-Temperature CO<sub>2</sub> Methanation. *Ind. Eng. Chem. Res.* 58 (20), 8656–8662. <https://doi.org/10.1021/acs.iecr.9b00983>.
- Liang, C., Hu, X., Wei, T., Jia, P., Zhang, Z., Dong, D., Zhang, S., Liu, Q., Hu, G., 2019. Methanation of CO<sub>2</sub> over Ni/Al<sub>2</sub>O<sub>3</sub> modified with alkaline earth metals: Impacts of oxygen vacancies on catalytic activity. *Int. J. Hydrog. Energy* 44 (16), 8197–8213. <https://doi.org/10.1016/j.ijhydene.2019.02.014>.
- Lim, J.Y., McGregor, J., Sederman, A.J., Dennis, J.S., 2016. Kinetic studies of CO<sub>2</sub> methanation over a Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst using a batch reactor. *Chem. Eng. Sci.* 141, 28–45. <https://doi.org/10.1016/j.ces.2015.10.026>.
- Ma, H., Ma, K., Ji, J., Tang, S., Liu, C., Jiang, W., Yue, H., Liang, B., 2019. Graphene intercalated Ni-SiO<sub>2</sub>/GO-Ni-foam catalyst with enhanced reactivity and heat-transfer for CO<sub>2</sub> methanation. *Chem. Eng. Sci.* 194, 10–21. <https://doi.org/10.1016/j.ces.2018.05.019>.
- Macdonald, I.R., Howe, R.F., Zhang, X., Zhou, W., 2010. In situ EPR studies of electron trapping in a nanocrystalline rutile. *J. Photoch. Photobiol. A* 216 (2–3), 238–243. <https://doi.org/10.1016/j.jphotochem.2010.07.023>.
- Miao, B., Ma, S.S.K., Wang, X., Su, H., Chan, S.H., 2016. Catalysis mechanisms of CO<sub>2</sub> and CO methanation. *Catal. Sci. Technol.* 6 (12), 4048–4058. <https://doi.org/10.1039/C6CY00478D>.
- Mohanakrishna, G., Vanbroekhoven, K., Pant, D., 2018. Impact of dissolved carbon dioxide concentration on the process parameters during its conversion to acetate through microbial electrosynthesis. *React. Chem. Eng.* 3 (3), 371–378. <https://doi.org/10.1039/C7RE00220C>.
- Murphy, D., Massiani, P., Franck, R., Barthomeuf, D., 1996. Basic site heterogeneity and location in alkali cation exchanged EMT zeolite. An IR study using adsorbed pyrrole. *J. Phys. Chem.* 100 (16), 6731–6738. <https://doi.org/10.1021/jp953383+>.
- Narayanan, S., Vijaya, J.J., Sivasanker, S., Alam, M., Tamizhdurai, P., Kennedy, L.J., 2015. Characterization and catalytic reactivity of mordenite–investigation of selective oxidation of benzyl alcohol. *Polyhedron* 89, 289–296. <https://doi.org/10.1016/j.poly.2014.12.038>.
- Pan, Q., Peng, J., Sun, T., Wang, S., Wang, S., 2014. Insight into the reaction route of CO<sub>2</sub> methanation: Promotion effect of medium basic sites. *Catal. Commun.* 45, 74–78. <https://doi.org/10.1016/j.catcom.2013.10.034>.
- Pang, H., Wang, X., Zhang, G., Chen, H., Lv, G., Yang, S., 2010. Characterization of diamond-like carbon films by SEM, XRD and Raman spectroscopy. *Appl. Surf. Sci.* 256 (21), 6403–6407. <https://doi.org/10.1016/j.apsusc.2010.04.025>.
- Park, J.N., McFarland, E.W., 2009. A highly dispersed Pd-Mg/SiO<sub>2</sub> catalyst active for methanation of CO<sub>2</sub>. *J. Catal.* 266 (1), 92–97. <https://doi.org/10.1016/j.jcat.2009.05.018>.
- Polshettiwar, V., Cha, D., Zhang, X., Basset, J.M., 2010. High-surface-area silica nanospheres (KCC-1) with a fibrous morphology. *Angew. Chem. Int. Ed.* 49 (50), 9652–9656. <https://doi.org/10.1002/anie.201003451>.
- Prapainainar, P., Maliwan, S., Sarakham, K., Du, Z., Prapainainar, C., Holmes, S.M., Kongkachuichay, P., 2018. Homogeneous polymer/filler composite membrane by spraying method for enhanced direct methanol fuel cell performance. *Int. J. Hydrog. Energy* 43 (31), 14675–14690. <https://doi.org/10.1016/j.ijhydene.2018.05.173>.
- Prapainainar, P., Pattanapisutkun, N., Prapainainar, C., Kongkachuichay, P., 2019. Incorporating graphene oxide to improve the performance of Nafion-mordenite composite membranes for a direct methanol fuel cell. *Int. J. Hydrog. Energy* 44 (1), 362–378. <https://doi.org/10.1016/j.ijhydene.2018.08.008>.
- Prymak, I., Kalevaru, V.N., Wohlrab, S., Martin, A., 2015. Continuous synthesis of diethyl carbonate from ethanol and CO<sub>2</sub> over Ce-Zr-O. *Catal. Sci. Technol.* 5 (4), 2322–2331. <https://doi.org/10.1039/C4CY01400F>.
- Qin, Z., Wang, X., Dong, L., Su, T., Li, B., Zhou, Y., Jiang, Y., Luo, X., Ji, H., 2019. CO<sub>2</sub> methanation on Co/TiO<sub>2</sub> catalyst: Effects of Y on the support. *Chem. Eng. Sci.* 210, 115245. <https://doi.org/10.1016/j.ces.2019.115245>.
- Radtke, A., Piszczek, P., Topolski, A., Lewandowska, Z., Talik, E., Andersen, I.H., Nielsen, L.P., Heikkilä, M., Leskela, M., 2016. The structure and the photocatalytic activity of Titania based nanotube and nanofiber coatings. *Appl. Surf. Sci.* 368, 165–172. <https://doi.org/10.1016/j.apsusc.2016.01.219>.
- Sanz-Perez, E.S., Murdock, C.R., Didas, S.A., Jones, C.W., 2016. Direct capture of CO<sub>2</sub> from ambient air. *Chem. Rev.* 116 (19), 11840–11876. <https://doi.org/10.1021/acs.chemrev.6b00173>.
- Shahul Hamid, M.Y., Triwahyono, S., Jalil, A.A., Che Jusoh, N.W., Izan, S.M., Tuan Abdullah, T.A., 2018. Tailoring the properties of metal oxide loaded/KCC-1 toward a different mechanism of CO<sub>2</sub> methanation by in situ IR and ESR. *Inorg. Chem.* 57 (10), 5859–5869. <https://doi.org/10.1021/acs.inorgchem.8b00241>.
- Su, X., Xu, J., Liang, B., Duan, H., Hou, B., Huang, Y., 2016. Catalytic carbon dioxide hydrogenation to methane: A review of recent studies. *J. Energy Chem.* 25 (4), 553–565. <https://doi.org/10.1016/j.jechem.2016.03.009>.
- Tada, S., Oshima, K., Noda, Y., Kikuchi, R., Sohmiya, M., Honma, T., Satokawa, S., 2019. Effects of Cu Precursor Types on the Catalytic Activity of Cu/ZrO<sub>2</sub> toward Methanol Synthesis via CO<sub>2</sub> Hydrogenation. *Ind. Eng. Chem. Res.* 58 (42), 19434–19445. <https://doi.org/10.1021/acs.iecr.9b03627>.
- Teh, L.P., Triwahyono, S., Jalil, A.A., Firmansyah, M.L., Mamat, C.R., Majid, Z.A., 2016. Fibrous silica mesoporous ZSM-5 for carbon monoxide methanation. *Appl. Catal. A: Gen.* 523, 200–208. <https://doi.org/10.1016/j.apcata.2016.05.031>.

- Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S., 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* 87 (9–10), 1051–1069. <https://doi.org/10.1515/pac-2014-1117>.
- Upham, D.C., Derk, A.R., Sharma, S., Metiu, H., McFarland, E.W., 2015. CO<sub>2</sub> methanation by Ru-doped ceria: the role of the oxidation state of the surface. *Catal. Sci. Technol.* 5 (3), 1783–1791. <https://doi.org/10.1039/C4CY01106F>.
- Vitiello, M., Lopez, N., Illas, F., Pacchioni, G., 2000. H<sub>2</sub> cracking at SiO<sub>2</sub> defect centers. *J. Phys. Chem. A* 104 (20), 4674–4684. <https://doi.org/10.1021/jp993214f>.
- Vogelaar, B.M., van Langeveld, A.D., Eijssbouts, S., Moulijn, J.A., 2007. Analysis of coke deposition profiles in commercial spent hydroprocessing catalysts using Raman spectroscopy. *Fuel* 86 (7–8), 1122–1129. <https://doi.org/10.1016/j.fuel.2006.10.002>.
- Wang, F., He, S., Chen, H., Wang, B., Zheng, L., Wei, M., Evans, D.G., Duan, X., 2016. Active site dependent reaction mechanism over Ru/CeO<sub>2</sub> catalyst toward CO<sub>2</sub> methanation. *J. Am. Chem. Soc.* 138 (19), 6298–6305. <https://doi.org/10.1021/jacs.6b02762>.
- Widmann, D., Leppelt, R., Behm, R.J., 2007. Activation of a Au/CeO<sub>2</sub> catalyst for the CO oxidation reaction by surface oxygen removal/oxygen vacancy formation. *J. Catal.* 251 (2), 437–442. <https://doi.org/10.1016/j.jcat.2007.07.026>.
- Xu, H., Zhang, Y., Wu, H., Liu, Y., Li, X., Jiang, J., He, M., Wu, P., 2011. Postsynthesis of mesoporous MOR-type titanosilicate and its unique catalytic properties in liquid-phase oxidations. *J. Catal.* 281 (2), 263–272. <https://doi.org/10.1016/j.jcat.2011.05.009>.
- Yu, Q., Sun, H., Sun, H., Li, L., Zhu, X., Ren, S., Guo, Q., Shen, B., 2019. Highly mesoporous IM-5 zeolite prepared by alkaline treatment and its catalytic cracking performance. *Micropor. Mesopor. Mat.* 273, 297–306. <https://doi.org/10.1016/j.micromeso.2018.08.016>.
- Zelenak, V., Zelenakova, A., Kovac, J., 2010. Insight into surface heterogeneity of SBA-15 silica: Oxygen related defects and magnetic properties. *Colloid Surf. A* 357 (1–3), 97–104. <https://doi.org/10.1016/j.colsurfa.2010.01.001>.
- Zhang, W., Machida, H., Takano, H., Izumiya, K., Norinaga, K., 2020. Computational fluid dynamics simulation of CO<sub>2</sub> methanation in a shell-and-tube reactor with multiphase coupled heat transfer. *Chem. Eng. Sci.* 211, 115276. <https://doi.org/10.1016/j.ces.2019.115276>.