



## Article Oxidative Coupling of Methane over Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiC Catalysts

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**Abstract:** The oxidative coupling of methane (OCM) is operated at high temperatures and is a highly exothermic reaction; thus, hotspots form on the catalyst surface during reaction unless the produced heat is removed. It is crucial to control the heat formed because surface hotspots can degrade catalytic performance. Herein, we report the preparation of Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiC catalysts using SiC, which has high thermal conductivity and good stability at high temperatures, and the catalyst was applied to the OCM. Two Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiC catalysts were prepared by wet-impregnation on SiC supports having different particle sizes. For comparison, the Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst was also prepared by the same method. The catalysts were analyzed by nitrogen adsorption-desorption, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The transformation of SiC into  $\alpha$ -cristobalite was observed for the Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiC catalysts. Because SiC was completely converted into  $\alpha$ -cristobalite for the nano-sized SiC-supported Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub> catalyst, the catalytic performance for the OCM reaction of Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/n-SiC was similar to that of  $Mn_2O_3-Na_2WO_4/SiO_2$ . However, only the surface layer of SiC was transformed into  $\alpha$ -cristobalite for the micro-sized SiC (m-SiC) in  $Mn_2O_3$ - $Na_2WO_4$ /m-SiC, resulting in a SiC@ $\alpha$ -cristobalite core-shell structure. The Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/m-SiC showed higher methane conversion and C<sub>2+</sub> yield at 800 and  $850 \degree C$  than  $Mn_2O_3$ - $Na_2WO_4/SiO_2$ .

**Keywords:** oxidative coupling of methane; Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiC; thermal conductive material; silicon carbide

#### 1. Introduction

Recently, the utilization of natural gas as a chemical feedstock has drawn attention because of the increased production of shale gas, a new and abundant gas resource [1–3]. Because the main component of shale gas is methane, research into the conversion of methane into value-added chemicals is actively underway. However, the direct conversion of methane into other chemicals is not easy because of its strong C-H bonds. Therefore, methane is currently converted into syngas (CO/H<sub>2</sub>) first by reforming [4,5] or partial oxidation [6–9], and subsequently, into bulk chemicals through secondary

chemical processes, such as the Fisher–Tropsch reaction [10–12], methanol synthesis [13–15], and dimethyl ether (DME) production [16,17] processes.

Because syngas synthesis via steam reforming consumes significant energy, much attention has been paid to the direct methane conversion technologies, such as the direct oxidation of methane into methanol or the oxidative coupling of methane (OCM) into olefins. The OCM reaction has drawn particular attention because olefins, such as ethylene and propylene, can be synthesized from methane directly without any intermediates, such as methanol or DME. However, the one-pass yield is still low, so the development of highly active catalyst for the OCM reaction is required. Some representative OCM catalysts are  $Mn_2O_3/Na_2WO_4/SiO_2$  [18–20], Li/MgO [21,22], and La<sub>2</sub>O<sub>3</sub>/CaO [23,24]. Of these,  $Mn_2O_3-Na_2WO_4/SiO_2$  has been reported to exhibit high catalytic activity and stability.

The following reactions can occur under OCM reaction conditions.

$$\begin{array}{ll} CH_4 + 3/2O_2 \rightarrow CO + 2H_2O & \Delta H^0_{298K} = -519 \text{ kJ/mol} \\ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O & \Delta H^0_{298K} = -802 \text{ kJ/mol} \\ CH_4 + 1/2O_2 \rightarrow 1/2C_2H_4 + H_2O & \Delta H^0_{298K} = -141 \text{ kJ/mol} \\ CH_4 + 1/4O_2 \rightarrow 1/2C_2H_6 + 1/2H_2O & \Delta H^0_{298K} = -88 \text{ kJ/mol} \end{array}$$

Because most reactions involved in the OCM are highly exothermic, hotspots can be easily formed in the catalyst layer. Therefore, the control of the reaction heat is a very important issue, although the development of the catalyst to improve the C<sub>2</sub> yields is also important [25,26]. Schweer et al. studied the formation of hotspots according to the reaction conditions in the OCM reaction over a La<sub>2</sub>O<sub>3</sub>/CaO catalyst [27]. They reported that the concentration of oxygen greatly influenced the formation of hotspots. Pak et al. reported that the OCM reaction over Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> and Mn/Na<sub>2</sub>WO<sub>4</sub>/MgO resulted in a relatively narrow hotspot region, producing temperature increases as large as 150 °C [28]. Because the formation of hotspots during the OCM reaction lowers the catalytic performance, such as olefin selectivity and catalyst lifetime, the effective control of the reaction heat is especially important for this reaction. Thus, a support with high thermal conductivity is required to resolve this hotspot issue because the formed heat can be removed easily through the catalyst bed.

Silicon carbide (SiC) has some interesting properties, such as its stability at high temperatures, high thermal conductivity, and chemical inertness, which enables SiC to be used as a support for heterogeneous catalysts [29–32]. There have been some reports on the application of SiC as a substrate for OCM reactions. Liu et al. studied hotspots of 5%Na2WO4-2%Mn/SiC monolithic foam and 5%Na<sub>2</sub>WO<sub>4</sub>-2%Mn/SiO<sub>2</sub> during the OCM reaction [33]. The temperature profiles of the two catalysts showed that the temperature increase of 5%Na<sub>2</sub>WO<sub>4</sub>-2%Mn/SiC catalyst bed was less than that of 5%Na<sub>2</sub>WO<sub>4</sub>-2%Mn/SiO<sub>2</sub> because of the high thermal conductivity of SiC. Wang et al. prepared an Mn/Na/W catalyst supported on nano-sized SiC and calcined it in either air or nitrogen [34]. They observed that calcination in nitrogen was more beneficial for preserving the high surface area of the catalyst than calcination in air. However, all these catalysts showed lower catalytic activity for OCM than Mn/Na/W/SiO<sub>2</sub>. Yildiz et al. also reported that  $Mn_xO_y$ -Na<sub>2</sub>WO<sub>4</sub>/SiC was inferior to  $Mn_xO_y$ -Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> for the OCM reaction at 750 °C [35]. To the best of our knowledge, there is no previous report on the positive effect of SiC particulate supports on the OCM reaction and how to preserve the SiC under OCM reaction conditions to take advantage of its high thermal conductivity. In this study, we have investigated how to maintain the SiC structure by controlling the particle size of the SiC particles. We have found that the Mn/Na<sub>2</sub>WO<sub>4</sub> catalyst supported on micro-sized SiC retained the SiC core and showed a better catalytic activity than the conventional  $Mn_2O_3$ - $Na_2WO_4$ /SiO<sub>2</sub> catalyst in the temperature range of 800–850 °C.

#### 2. Results

#### 2.1. Catalyst Characterization

Figure 1a shows N<sub>2</sub> adsorption–desorption isotherms of the catalyst supports. The N<sub>2</sub> isotherm of SiO<sub>2</sub> shows a typical type-IV(a) isotherm with H1-type hysteresis loop at a relative pressure (*P*/*P*<sub>0</sub>) of ca. 0.4 [36], which indicates a mesoporous structure with an average pore size of 5.72 nm (Figure S1) and a large specific surface area (Table 1). On the other hand, the N<sub>2</sub> isotherm of nano-sized SiC (n-SiC) and micro-sized SiC (m-SiC) were observed at the bottom, indicating a very low surface area because of their non-porous structures (Figure S1). Table 1 summarizes the Brunauer–Emmett–Teller (BET) specific surface areas of the pristine supports, calcined supports, and supported Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub> (MNW) catalysts. The specific surface areas of pristine m-SiC, n-SiC, and SiO<sub>2</sub> were determined to be <1, 43, and 463 m<sup>2</sup>g<sup>-1</sup>, respectively. The n-SiC had a relatively larger specific surface area than the m-SiC because of its small particle size. The specific surface areas of n-SiC and SiO<sub>2</sub> were reduced to about half after calcination in air at 800 °C. They were further decreased significantly after loading with MNW and subsequent calcination in air at 800 °C. The N<sub>2</sub> adsorption–desorption isotherm data of the three catalysts were all observed at the bottom (Figure 1b). The specific surface areas of MNW/SiO<sub>2</sub> and MNW/n-SiC were determined to be 5 and 4 m<sup>2</sup>g<sup>-1</sup>, respectively. On the other hand, MNW/m-SiC showed a slightly increased specific surface area of 2 m<sup>2</sup>g<sup>-1</sup> compared with that of the pristine support.



Figure 1.  $N_2$  adsorption-desorption isotherm of (a) pristine support and (b) supported  $Mn_2O_3$ - $Na_2WO_4$  catalysts.

Specific Surface Area (m <sup>2</sup> ·g <sup>-1</sup> )		
Pristine	Treated at 800 $^\circ C$ $^a$	Supported MNW Catalyst <sup>b</sup>
<1	<1	2
43	24	4
463	264	5
	Pristine <1 43 463	Specific Surface And Pristine         Treated at 800 °C a           <1

Table 1. Specific surface areas of supports and supported Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub> catalysts.

Note: <sup>a</sup> Samples were calcined in air at 800  $^{\circ}$ C for 4 h; <sup>b</sup> supported Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub> catalysts were calcined in air at 800  $^{\circ}$ C for 4 h.

XRD data of the prepared catalysts (MNW/SiO<sub>2</sub>, MNW/n-SiC, and MNW/m-SiC) calcined in air at 800 °C were obtained and compared with those of each pristine support (Figure 2). The amorphous silica phase was confirmed to be SiO<sub>2</sub> based on the broad XRD peak at around 23°. The bulk phases of n-SiC and m-SiC were determined to be  $\beta$ -SiC and  $\alpha$ -SiC, respectively. After the loading of MNW onto each support, the characteristic XRD peaks corresponding to Mn<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>WO<sub>4</sub> were found in all catalyst samples. In the case of MNW/n-SiC and MNW/m-SiC, the XRD peak arising from graphite was detected at 26.6°, which was formed during the phase transformation of SiC in the calcination step. Notably, the main XRD peak arising from  $\alpha$ -cristobalite was observed for all catalyst samples at 22°. In general, the amorphous SiO<sub>2</sub> begins to crystallize at above 1500 °C, finally becoming

 $\alpha$ -cristobalite [37]. However, the crystallization of SiO<sub>2</sub> to  $\alpha$ -cristobalite was reported to be accelerated in the presence of Na at above 700 °C [38]. Note that the SiC in MNW/m-SiC and MNW/n-SiC was also transformed into  $\alpha$ -cristobalite, even though SiC has been reported to be thermally stable [34]. The XRD data show that the XRD peaks of SiO<sub>2</sub> in MNW/SiO<sub>2</sub> and  $\beta$ -SiC in MNW/n-SiC disappear, and a new intense XRD peak arising from  $\alpha$ -cristobalite appears (Figure 2c–f). However, XRD peaks arising from both  $\alpha$ -SiC and  $\alpha$ -cristobalite were detected in the XRD pattern of MNW/m-SiC (Figure 2a,b). This indicates that only the surface of m-SiC was oxidized for MNW/m-SiC because of the large particle size of m-SiC (ca. 14 µm). The crystallite sizes of  $\alpha$ -cristobalite of MNW/m-SiC, MNW/n-SiC, and MNW/SiO<sub>2</sub> were calculated to be 18, 31, and 31 nm, respectively, using the Debye–Scherrer equation. This indicates that SiC in MNW/m-SiC is less oxidized than that of MNW/n-SiC, which has a similar crystallite size to that of  $\alpha$ -cristobalite with MNW/SiO<sub>2</sub>.



Figure 2. X-ray diffraction patterns of (a) MNW/m-SiC; (b) m-SiC; (c) MNW/n-SiC; (d) n-SiC; (e) MNW/SiO<sub>2</sub>; and (f) SiO<sub>2</sub>.

Figure 3 shows scanning electron microscopy (SEM) images of the supports and supported MNW catalysts. The m-SiC particles are splinter-like, measuring several tens of microns in size and having a smooth surface (Figure 3a). In contrast, the particles of n-SiC measure several tens of nanometers (Figure 3c). SiO<sub>2</sub> is present as large particles of several hundred of microns in size, but the magnified inset image shows that the particles are composed of fine nanoparticles (Figure 3e). Upon the loading of Mn<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>WO<sub>4</sub> and subsequent calcination in air at 800 °C, there were significant morphological changes for each catalyst. The apparent particle size of MNW/SiO<sub>2</sub> appeared to be maintained at several hundreds of microns, but the nanoparticle structure on the surface disappeared to form a unique structure at the micrometer scale (Figure 3f). A similar phenomenon was also observed for MNW/n-SiC (Figure 3d). The nanoparticles in MNW/n-SiC were integrated into irregularly shaped micro-sized particles. On the other hand, the particles in MNW/m-SiC retained their micro-sized structure, but the particle surface changed from smooth to rough (Figure 3b). (Figure S2) The chemical composition of each catalyst was confirmed by SEM–energy dispersive X-ray (EDX) mapping, which reveals the presence of Si, Mn, Na, and W (Figure S2). Mn, Na, and W appear to be well dispersed in each catalyst. Figure S3a shows the transmission electron microscopy (TEM) image of MNW/m-SiC.

Because the core–shell structure was not clearly revealed in the TEM image, EDX line-scanning analysis was performed on the samples in the TEM equipment. Figure S3b shows the concentration profiles for Si, O, Na, W, and Mn along the line drawn on the TEM image of NWM/m-SiC (Figure S3a). Si was detected throughout the particle, O was mainly found in the shell of particle, and Mn, Na, and W were detected at low concentrations throughout the whole particle. Thus, we confirmed that surface oxidation of the m-SiC had occurred and that the core was composed of SiC, confirming the core–shell structure.



**Figure 3.** The scanning electron microscope (SEM) images of pristine supports and supported Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub> catalysts: (**a**) m-SiC; (**b**) MNW/m-SiC; (**c**) n-SiC; (**d**) MNW/n-SiC, (**e**) SiO<sub>2</sub>; and (**f**) MNW/SiO<sub>2</sub>.

#### 2.2. OCM Reaction

The catalytic activities for the OCM reaction, such as CH<sub>4</sub> conversion, C<sub>2+</sub> selectivity, C<sub>2+</sub> yield, and the  $C_2H_4/C_2H_6$  ratio, were evaluated over the supported NMW catalysts at different temperatures. Since  $C_{3+}$  yield was very low (<0.1%), the  $C_2H_4/C_2H_6$  ratio was calculated to represent the olefin to paraffin ratio. Except for  $C_{2+}$  compounds, only CO and  $CO_2$  were detected as the side products. As shown in Figure 4, the catalytic activity of NWM/n-SiC showed a similar trend to that of NWM/SiO<sub>2</sub>. The CH<sub>4</sub> conversions over NMW/SiO<sub>2</sub> and NMW/n-SiC were in the range of 30–33% in the temperature range from 750 to 850 °C. NMW/n-SiC showed slightly higher CH<sub>4</sub> conversions than NMW/SiO<sub>2</sub> at above 800 °C (Figure 4a). On the other hand, the C<sub>2+</sub> selectivity of MNW/n-SiC was about 53%, which is slightly lower than that of MNW/SiO<sub>2</sub> (Figure 4b). As a result, the  $C_{2+}$  yield of NMW/n-SiC was lower than that of NMW/SiO<sub>2</sub> at 750 °C, and the difference in  $C_{2+}$  yield decreased with increasing reaction temperature (Figure 4d). A similar trend was also observed in the  $C_2H_4/C_2H_6$  ratios over NWM/n-SiC and NWM/SiO<sub>2</sub>. This is closely related to the phase transformation of  $\beta$ -SiC into  $\alpha$ -cristobalite for MNW/n-SiC in the calcination step. Both Mn/SiO<sub>2</sub> and Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> were reported to be active for OCM reaction [18]. Especially, the presence of Na was reported to induce a phase transform of  $SiO_2$  to  $\alpha$ -cristobalite during the calcination. However, because the  $\alpha$ -cristobalite causes high selectivity of C<sub>2</sub> in OCM reaction, the Na is important for serving as a structural and chemical promoter [18]. There is no significant difference in the physical properties, such as the specific surface area,  $\alpha$ -cristobalite crystallite size, and bulk crystalline phase between NWM/n-SiC and NWM/SiO<sub>2</sub>. On the other hand, MNW/m-SiC showed a different catalytic activity trend as a function of temperature compared with

NWM/n-SiC and NWM/SiO<sub>2</sub>. The CH<sub>4</sub> conversion was 12.4% at 750 °C over MNW/m-SiC, which is much lower than that of NWM/SiO<sub>2</sub>. However, the CH<sub>4</sub> conversion increased with increasing reaction temperature, to 33.6% at 800 °C, which is comparable to that of NWM/SiO<sub>2</sub>. Note that the O<sub>2</sub> conversions over MNW/m-SiC at 750 °C and 800 °C were 41% and 98%, respectively. These values are much lower than those of NWM/n-SiC and NWM/SiO<sub>2</sub>, which showed complete O<sub>2</sub> conversion at all reaction temperatures. MNW/m-SiC showed much higher C<sub>2+</sub> selectivity than NWM/SiO<sub>2</sub> at all reaction temperatures, resulting in the highest C<sub>2+</sub> yield at 800 and 850 °C among three catalysts. Compared with the MNW/SiO<sub>2</sub> catalyst, the MNW/m-SiC catalyst showed higher catalytic activities for the OCM reaction at high temperatures, despite its lower specific surface area (Table 1). In the case of MNW/m-SiC, the phase transformation of  $\alpha$ -SiC into  $\alpha$ -cristobalite only occurred on the surface of the SiC particles, resulting in the SiC@ $\alpha$ -cristobalite core–shell structure. The catalytic activity for the OCM reaction is expected to increase because of the excellent thermal conductivity of the SiC core present in the MNW/m-SiC. Liu et al. [33] reported that hotspots were not formed during the OCM reaction in a 5%Na<sub>2</sub>WO<sub>4</sub>-2%Mn/SiC-monolith foam, unlike 5% Na<sub>2</sub>WO<sub>4</sub>-2% Mn/SiO<sub>2</sub>.



**Figure 4.** The catalytic activity for OCM reaction over MNW/n-SiC, MNW/m-SiC, and MNW/SiO<sub>2</sub> catalysts as a function of temperature. (a) CH<sub>4</sub> conversion; (b) C<sub>2+</sub> selectivity; (c) C<sub>2+</sub> yield; and (d) C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio (feed composition: CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> = 3/1/1, GHSV =  $10,000 h^{-1}$ ).

The catalytic activity for the OCM reaction over MNW/m-SiC was monitored at 800 °C for 10 h. Figure 5 shows the CH<sub>4</sub> conversion, C<sub>2+</sub> selectivity, C<sub>2+</sub> yield, and ratio of C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> with time on stream. The stable CH<sub>4</sub> conversion was achieved during the stability test, and the steady-state CH<sub>4</sub> conversion was about 37.5% (Figure 5a). The C<sub>2+</sub> selectivity was also maintained at about 54.5% (Figure 5b). The C<sub>2+</sub> yield and the ratio of C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> at steady state were 20.5% and 2.3, respectively (Figure 5c,d). To identify any changes in the bulk structure of the MNW/m-SiC catalyst during the stability tests, XRD patterns for the MNW/m-SiC catalysts before and after the stability test were compared, as shown in Figure 6. XRD peaks corresponding to  $\alpha$ -SiC are present in the XRD peak arising from

 $\alpha$ -cristobalite increased slightly after the stability tests. This indicates that a further transformation of SiC into  $\alpha$ -cristobalite occurred during the stability test.



**Figure 5.** The catalytic activity for OCM reaction over MNW/m-SiC catalyst at 800 °C with time-on stream. (a) CH<sub>4</sub> conversion; (b) C<sub>2+</sub> selectivity; (c) C<sub>2+</sub> yield; and (d) C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio (feed composition: CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> = 3/1/1, GHSV = 10,000 h<sup>-1</sup>).



**Figure 6.** X-ray diffraction patterns for the fresh and spent MNW/m-SiC samples. The reaction conditions are same as described in Figure 6.

The SiC of NWM/SiC can contribute to the OCM performance by removing heat easily because of its excellent thermal conductivity. However, the oxidation of SiC is promoted by the presence of Na in the catalyst, resulting in the formation of  $\alpha$ -cristobalite with a very low specific surface area. In the case of n-SiC, even though it has a large specific surface area, it is easily oxidized when used as

a support for NWM/n-SiC. Therefore, there is no noticeable difference in the catalytic performance between MNW/SiO<sub>2</sub> and MNW/n-SiC. However, the SiC in the MNW/m-SiC catalyst remained in the core, even though the surface SiC layer was transformed into  $\alpha$ -cristobalite. This is beneficial for the OCM reaction at high temperatures and explains its better performance compared with MNW/SiO<sub>2</sub>.

#### 3. Materials and Methods

#### 3.1. Materials

Two SiC supports with particle sizes of 45–65 nm and 14  $\mu$ m were purchased from US Research Nanomaterials and Alfa Aesar, respectively. These SiC samples are denoted n-SiC and m-SiC, respectively. SiO<sub>2</sub> (Alfa Aesar, Haverhill, MA, USA), Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Kanto Chemical, Tokyo, Japan), and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (Yakuri Pure Chemicals, Kyoto, Japan) were used as received.

#### 3.2. Catalyst Preparation

The 5 wt% Na<sub>2</sub>WO<sub>4</sub> and 2 wt% Mn supported on n-SiC or m-SiC were prepared by a wet impregnation method. First, 0.15 mL of Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution and 0.14 g of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were dissolved in 100 mL of distilled water; then, 2.34 g of SiC was added to the aqueous solution and stirred at 60 °C for 4 h. The supported catalyst was dried at 105 °C overnight and then calcined in air at 800 °C for 5 h before the activity test. For comparison, the Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> was also prepared by the same method. For brevity, the Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/n-SiC, Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/m-SiC, and Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalysts are denoted MNW/n-SiC, MNW/m-SiC, and MNW/SiO<sub>2</sub>, respectively.

#### 3.3. Catalyst Characterization

The bulk structure of the prepared catalysts was analyzed by XRD (XRD-6000, Shimadzu, Kyoto, Japan) using monochromatic Cu- $K_{\alpha}$  ( $\lambda = 0.15406$  nm) radiation. The X-rays were generated at 40 kV and 30 mA, and the XRD patterns were obtained at a scan rate of  $0.02^{\circ}$ /s. The specific surface area and pore size distribution of samples were measured by nitrogen adsorption–desorption analysis (ASAP2010 physisorption apparatus, Micromeritics, Norcross, GA, USA) after degassing under vacuum at 200 °C for 4 h. The specific surface area and pore size distribution of the catalyst were calculated using the BET and Barrett–Joyner–Halenda (BJH) method, respectively. The surface morphology of the samples was observed by field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Tokyo, Japan). The structure was also characterized by field emission transmission electron microscopy (FE-TEM, Tecnai G2 F30 S-Twin, FEI, Hilsboro, OR, USA) operated at 300 kV. The chemical compositions of structure were analyzed by TEM equipped with EDX equipment for line analysis.

#### 3.4. Reaction Procedure

The OCM reaction was conducted in a fixed-bed quartz reactor (inlet diameter: 6 mm, outlet diameter: 1 mm) at atmospheric pressure; 0.18 mL of the calcined catalyst was fixed on quartz wool in the middle of the reactor. The reaction was carried out in the temperature range of 750–800 °C with a gas hourly space velocity (GHSV) of 10,000 h<sup>-1</sup>. The weight hourly space velocity (WHSV) of MNW/m-SiC, MNW/n-SiC, and MNW/SiO<sub>2</sub> were  $1.59 \times 10^4$ ,  $1.79 \times 10^4$ , and  $3.31 \times 10^4$  mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>, respectively. The temperature was controlled by the furnace set temperature. The molar ratio of CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> was fixed as 3/1/1 in the feed stream. The water produced during the reaction was removed using a condenser at the end of the reactor, and the gas products were separated with HP-PLOT Al<sub>2</sub>O<sub>3</sub> S and Carboxen 1000 columns in a gas chromatograph (7890A, Agilent, Santa Clara, CA, USA) and then analyzed with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The conversion of methane and the selectivity and yield of C<sub>2+</sub> products were calculated as follows.

$$CH_4 Conversion (\%) = \frac{\text{moles of } CH_4 \text{ consumed}}{\text{moles of } CH_4 \text{ in the feed}} \times 100$$
(1)

$$C_{2+} \text{ Selectivity } (\%) = \frac{2 \times \text{moles of } C_2 \text{ hydrocarbons} + 3 \times \text{moles of } C_3 \text{ hydrocarbons}}{\text{moles of } CH_4 \text{ consumed}} \times 100$$
(2)  
$$C_{2+} \text{ Viold } (\%) = \frac{CH_4 \text{ Conversion} \times C_{2+} \text{ Selectivity}}{(3)}$$

# $C_{2+} \text{ Yield } (\%) = \frac{CH_4 \text{ Conversion} \times C_{2+} \text{ Selectivity}}{100}$ (3)

#### 4. Conclusions

Silicon carbide, which has high thermal conductivity, was applied to the highly exothermic OCM reaction as the support for the  $Mn_2O_3$ - $Na_2WO_4$  catalyst. Although the SiC was stable after calcination in air at 800 °C, the surface of the SiC was oxidized to  $\alpha$ -cristobalite after the impregnation of the active components ( $Mn_2O_3$ - $Na_2WO_4$ ) on the SiC. The degree of oxidation of SiC in the  $Mn_2O_3$ - $Na_2WO_4$ /SiC catalyst was dependent on the particle size of SiC. The complete transformation of SiC into  $\alpha$ -cristobalite was confirmed for nano-sized SiC (n-SiC) in  $Mn_2O_3$ - $Na_2WO_4$ /n-SiC. However, the surface oxidation of SiC was observed for micro-sized SiC (m-SiC) in  $Mn_2O_3$ - $Na_2WO_4$ /m-SiC, resulting in the SiC@ $\alpha$ -cristobalite core–shell structure. The methane conversion and  $C_{2+}$  yield of MNW/n-SiC were similar to those of MNW/SiO<sub>2</sub> because the SiC was completely transformed into  $\alpha$ -cristobalite in the catalyst preparation step. On the other hand, MNW/m-SiC, which retained a SiC core, showed higher methane conversion and  $C_{2+}$  yield at 800 and 850 °C than MNW/SiO<sub>2</sub>. Therefore, the SiC with a suitable particle size is a promising candidate as a catalyst support, even under highly oxidizing reaction conditions, while taking advantage of the facile heat transfer across the catalyst particles in the bed, which is essential for resolving the hotspot issues in highly exothermic reactions, including the OCM reaction.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/9/4/363/s1. Figure S1: Pore size distribution of supports, such as n-SiC, m-SiC, and SiO<sub>2</sub>. Figure S2: SEM-EDX mapping of (a) MNW/n-SiC, (b) MNW/m-SiC, and (c) MNW/SiO<sub>2</sub>. Figure S3: (a) TEM image and (b) TEM-EDX line concentration profiles for Si, O, Na, W, and Mn along a line drawn across the TEM of MNW/m-SiC. Table S1: Specific surface area, average pore diameter, and pore volume of supported Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub> catalysts.

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#### References

- 1. Wang, Q.; Chen, X.; Jha, A.N.; Rogers, H. Natural gas from shale formation–the evolution, evidences and challenges of shale gas revolution in United States. *Renew. Sust. Energ. Rev.* **2014**, *30*, 1–28. [CrossRef]
- 2. Jiyao, G.; You, F. Design and optimization of shale gas energy systems: Overview, research challenges, and future directions. *Comput. Chem. Eng.* **2017**, *106*, 699–718.
- 3. Middleton, R.S.; Gupta, R.; Hyman, J.D.; Viswanathan, H.S. The shale gas revolution: Barriers, sustainability, and emerging opportunities. *Appl. Energy* **2017**, *199*, 88–95. [CrossRef]
- Vita, A.; Cristiano, G.; Italiano, C.; Specchia, S.; Cipitì, F.; Specchia, V. Methane oxy-steam reforming reaction: Performances of Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalysts loaded on structured cordierite monoliths. *Int. J. Hydrog. Energy* 2014, 39, 18592–18603. [CrossRef]
- Villoria, J.A.; Alvarez-Galvan, M.C.; Al-Zahrani, S.M.; Palmisano, P.; Specchia, S.; Specchia, V.; Fierro, J.L.G.; Navarro, R.M. Oxidative reforming of diesel fuel over LaCoO<sub>3</sub> perovskite derived catalysts: Influence of perovskite synthesis method on catalyst properties and performance. *Appl. Catal. B Environ.* 2011, 105, 276–288. [CrossRef]
- 6. Ashcroft, A.T.; Cheetham, A.K.; Green, M.; Vernon, P.D.F. Partial oxidation of methane to synthesis gas using carbon dioxide. *Nature* **1991**, *352*, 225. [CrossRef]

- Singha, R.K.; Ghosh, S.; Acharyya, S.S.; Yadav, A.; Shukla, A.; Sasaki, T.; Venezia, A.M.; Pendem, C.; Bal, R. Partial oxidation of methane to synthesis gas over Pt nanoparticles supported on nanocrystalline CeO<sub>2</sub> catalyst. *Catal. Sci. Technol.* 2016, *6*, 4601–4615. [CrossRef]
- 8. Consuelo, A.G.; Mayra, M.; Laura, R.M.; Jose, L.E.; Rufino, M.N.; Mahdi, A.; Beatriz, R.C.; Jose, L.G.F. Partial Oxidation of Methane to Syngas Over Nickel-Based Catalysts: Influence of Support Type, Addition of Rhodium, and Preparation Method. *Front. Chem.* **2019**, *7*, 104.
- 9. Vella, L.D.; Villoria, J.A.; Specchia, S.; Mota, N.; Fierro, J.L.G.; Specchia, V. Catalytic partial oxidation of CH<sub>4</sub> with nickel–lanthanum-based catalysts. *Catal. Today* **2011**, *171*, 84–96. [CrossRef]
- 10. Cheng, Q.; Tian, Y.; Lyu, S.; Zhao, N.; Ma, K.; Ding, T.; Jiang, Z.; Wang, L.; Zhang, J.; Zheng, L.; et al. Confined small-sized cobalt catalysts stimulate carbon-chain growth reversely by modifying ASF law of Fischer–Tropsch synthesis. *Nature Commun.* **2018**, *9*, 3250. [CrossRef]
- 11. Aluha, J.; Hu, Y.; Abatzoglou, N. Effect of CO concentration on the α-value of plasma-synthesized Co/C catalyst in Fischer-Tropsch synthesis. *Catalysts* **2017**, *7*, 69. [CrossRef]
- 12. Davis, B.H.; Occelli, M.L. *Fischer-Tropsch Synthesis, Catalysts and Catalysis;* Elsevier: Amsterdam, The Netherlands, 2006.
- 13. da Silva, M.J. Synthesis of methanol from methane: Challenges and advances on the multi-step (syngas) and one-step routes (DMTM). *Fuel Process. Technol.* **2016**, 145, 42–61. [CrossRef]
- 14. Kuld, S.; Thorhauge, M.; Falsig, H.; Elkjær, C.F.; Helveg, S.; Chorkendorff, I.; Sehested, J. Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Science* **2016**, *352*, 969–974. [CrossRef]
- 15. Van Den Berg, R.; Prieto, G.; Korpershoek, G.; Van Der Wal, L.I.; Van Bunningen, A.J.; Lægsgaard-Jørgensen, S.; De Jongh, P.E.; De Jong, K.P. Structure sensitivity of Cu and CuZn catalysts relevant to industrial methanol synthesis. *Nature Commun.* **2016**, *7*, 13057. [CrossRef]
- Saravanan, K.; Ham, H.; Tsubaki, N.; Bae, J.W. Recent progress for direct synthesis of dimethyl ether from syngas on the heterogeneous bifunctional hybrid catalysts. *Appl. Catal. B: Environ.* 2017, 217, 494–522. [CrossRef]
- 17. Dadgar, F.; Myrstad, R.; Pfeifer, P.; Holmen, A.; Venvik, H.J. Direct dimethyl ether synthesis from synthesis gas: The influence of methanol dehydration on methanol synthesis reaction. *Catal. Today* **2016**, *270*, 76–84. [CrossRef]
- 18. Palermo, A.; Vazquez, J.P.; Lee, A.F.; Tikhov, M.S.; Lambert, R.M. Critical influence of the amorphous silica-to-cristobalite phase transition on the performance of Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalysts for the oxidative coupling of methane. *J. Catal.* **1998**, 177, 259–266. [CrossRef]
- 19. Elkins, T.W.; Hagelin-Weaver, H.E. Characterization of Mn–Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> and Mn–Na<sub>2</sub>WO<sub>4</sub>/MgO catalysts for the oxidative coupling of methane. *Appl. Catal. A: Gen.* **2015**, *497*, 96–106. [CrossRef]
- 20. Ahari, J.S.; Zarrinpashne, S.; Sadeghi, M.T. Micro-kinetic modeling of OCM reactions over Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst. *Fuel process. Technol.* **2013**, *115*, 79–87. [CrossRef]
- Arndt, S.; Laugel, G.; Levchenko, S.; Horn, R.; Baerns, M.; Scheffler, M.; Schlögl, R.; Schomäcker, R. A critical assessment of Li/MgO-based catalysts for the oxidative coupling of methane. *Catal. Rev.* 2011, 53, 424–514. [CrossRef]
- 22. Amin, N.A.S.; Pheng, S.E. Influence of process variables and optimization of ethylene yield in oxidative coupling of methane over Li/MgO catalyst. *Chem. Eng. J.* **2006**, *116*, 187–195. [CrossRef]
- 23. Rane, V.H.; Chaudhari, S.T.; Choudhary, V.R. Oxidative coupling of methane over La-promoted CaO catalysts: Influence of precursors and catalyst preparation method. *J. Nat. Gas Chem.* **2010**, *19*, 25–30. [CrossRef]
- 24. Stansch, Z.; Mleczko, L.; Baerns, M. Comprehensive kinetics of oxidative coupling of methane over the La<sub>2</sub>O<sub>3</sub>/CaO catalyst. *Ind. Eng. Chem. Res.* **1997**, *36*, 2568–2579. [CrossRef]
- 25. Vandewalle, L.A.; de Vijver, R.V.; Van Greem, K.M.; Marin, G.B. The role of mass and heat transfer in the design of novel reactors for oxidative coupling of methane. *Chem. Eng. Sci.* **2019**, *198*, 268–289. [CrossRef]
- Aseem, A.; Jeba, G.G.; Conato, M.T.; Rimer, J.D.; Harold, M.P. Oxidative coupling of methane over mixed metal oxide catalysts: Steady state multiplicity and catalyst durability. *Chem. Eng. J.* 2018, 331, 132–143. [CrossRef]
- 27. Schweer, D.; Meeczko, L.; Baerns, M. OCM in a fixed-bed reactor: Limits and perspectives. *Catal. Today* **1994**, 21, 357–369. [CrossRef]
- 28. Pak, S.; Lunsford, J.H. Thermal effects during the oxidative coupling of methane over Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> and Mn/Na<sub>2</sub>WO<sub>4</sub>/MgO catalysts. *Appl. Catal. A Gen.* **1998**, *168*, 131–137. [CrossRef]

- Le, T.A.; Kang, J.K.; Park, E.D. CO and CO<sub>2</sub> Methanation Over Ni/SiC and Ni/SiO<sub>2</sub> Catalysts. *Top. Catal.* 2018, *61*, 1537–1544. [CrossRef]
- 30. De la Osa, A.; Romero, A.; Dorado, F.; Valverde, J.; Sánchez, P. Influence of cobalt precursor on efficient production of commercial fuels over FTS Co/SiC. *Catalysts* **2016**, *6*, 98. [CrossRef]
- Ercolino, G.; Stelmachowski, P.; Specchia, S. Catalytic performance of Pd/Co<sub>3</sub>O<sub>4</sub> on SiC and ZrO2 open cell foams for process intensification of methane combustion in lean conditions. *Ind. Eng. Chem. Res.* 2017, 56, 6625–6636. [CrossRef]
- Liao, M.; Wang, C.; Bu, E.; Chen, Y.; Cheng, Z.; Luo, X.; Shu, R.; Wu, J. Efficient hydrogen production from partial oxidation of propane over SiC doped Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. *Energy Procedia* 2019, 158, 1772–1779. [CrossRef]
- Liu, H.; Yang, D.; Gao, R.; Chen, L.; Zhang, S.; Wang, X. A novel Na<sub>2</sub>WO<sub>4</sub>–Mn/SiC monolithic foam catalyst with improved thermal properties for the oxidative coupling of methane. *Catal. Commun.* 2008, *9*, 1302–1306. [CrossRef]
- 34. Wang, H.; Schmack, R.; Paul, B.; Albrecht, M.; Sokolov, S.; Rümmler, S.; Kondratenko, E.V.; Kraehnert, R. Porous silicon carbide as a support for Mn/Na/W/SiC catalyst in the oxidative coupling of methane. *Appl. Catal. A Gen.* **2017**, *537*, 33–39. [CrossRef]
- 35. Yildiz, M.; Simon, U.; Otremba, T.; Aksu, Y.; Kailasam, K.; Thomas, A.; Schomäcker, R.; Arndt, S. Support material variation for the Mn<sub>x</sub>O<sub>y</sub>-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst. *Catal. Today* **2014**, *228*, 5–14. [CrossRef]
- Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez–Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* 2015, *87*, 1051–1069. [CrossRef]
- 37. Breneman, R.C.; Halloran, J.W. Kinetics of cristobalite formation in sintered silica. *J. Am. Ceram. Soc.* 2004, 97, 2272–2278. [CrossRef]
- 38. Wu, J.; Li, S.; Niu, J.; Fang, X. Mechanistic study of oxidative coupling of methane over Mn<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>WO<sub>4</sub>SiO<sub>2</sub> catalyst. *Appl. Catal. A Gen.* **1995**, *124*, 9–18. [CrossRef]



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