

Robust microwave catalytic oxidative coupling of methane over $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$

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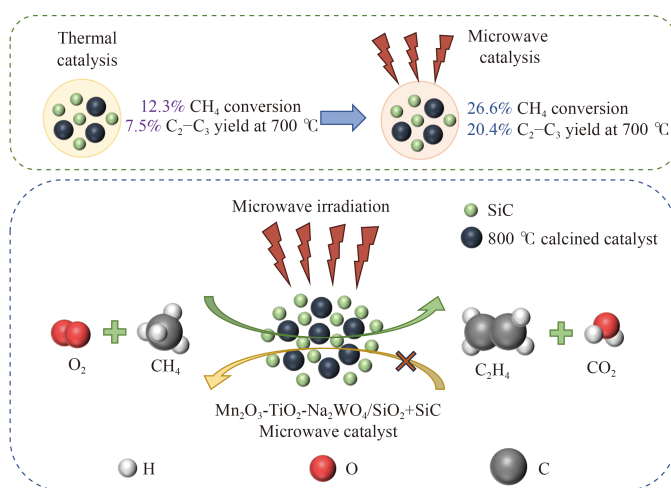
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Abstract: Oxidative coupling of methane (OCM) is an important way for the high-value utilization of methane (CH_4), but there are still some problems such as insufficient conversion and selectivity under traditional thermal catalysis. Herein, a new $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ microwave catalyst was developed for the oxidative coupling of methane under microwave irradiation. The results indicate that the calcined $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst is superior to the uncalcined counterpart in performance and the microwave catalytic reaction mode (MCRM) is significantly advantageous to the conventional reaction mode (CRM) for the OCM. For OCM at 700 °C in MCRM, the

conversion of CH_4 , the selectivity to $\text{C}_2\text{-C}_3$ hydrocarbons, and the yield of $\text{C}_2\text{-C}_3$ are 26.6%, 76.5% and 20.4%, respectively, much superior to the values of 12.3%, 61.9% and 7.5% in CRM under identical reaction conditions. That is, microwave irradiation can significantly enhance the yield of $\text{C}_2\text{-C}_3$ for OCM at a lower reaction temperature. The $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst shows favorable stability at 700 °C during the OCM reaction in MCRM for 20 h, with a methane conversion of above 25% and a selectivity of above 76% to $\text{C}_2\text{-C}_3$ hydrocarbons. Further study illustrates that the microwave irradiation can significantly reduce the apparent activation energy to 27.5 kJ/mol, compared with the value of 173 kJ/mol in the conventional mode, promote the free radical coupling and inhibit deep oxidation of OCM products. These results provide a new idea for the efficient conversion of CH_4 at a low temperature and for the sustainable development of green chemical industry.

Key words: microwave catalysis; low temperature and high efficiency; $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$; oxidative coupling of methane



$\text{C}_2\text{-C}_3$ hydrocarbons are essential raw materials in the chemical industry, conventionally derived from the high-energy processing of crude oil^[1]. In recent years, gas conversion aimed at developing sustainable alternatives has received increasing attention^[2-3]. Although traditional methods predominantly proceed through the indirect syngas route, the direct conversion of methane (CH_4) to $\text{C}_2\text{-C}_3$

hydrocarbons is considered a more attractive approach^[4-5]. Methane can be transformed into high-value fuels and chemicals through either non-oxidative or oxidative catalytic routes^[6-8]; among them, the non-oxidative pathway demonstrates high $\text{C}_2\text{-C}_3$ selectivity and atomic efficiency. However, it requires endothermic operation at a temperature up to 1100 °C, resulting in significant energy consumption

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and CO₂ emission^[2]. In contrast, the methane oxidative coupling (OCM) reaction directly converts methane into C₂–C₃ hydrocarbons in a single step^[9], offering the advantages of a shortened pathway with high energy efficiency, which is considered a cutting-edge technology for the high-value utilization of natural gas^[10–11]. However, the OCM reaction still faces challenges including the difficulty in methane activation^[12] and the severe deep oxidation of products^[13], which hinder the balance between conversion and selectivity. This imbalance has long been recognized as a persistent challenge in this field. Therefore, the high-efficient implementation of OCM is not only the core issue in the high-value utilization of natural gas, but also an important direction for advancing the clean conversion of CH₄ resources, alleviating energy pressures, and promoting the sustainable development of the green chemical industry^[14].

The OCM reaction represents a promising and practical pathway for the chemical utilization of methane^[15–17]. Various catalysts have been reported for the OCM reaction, among which Mn–Na₂WO₄/SiO₂ is regarded as the most promising one^[15–20]. These catalysts typically exhibit good stability and C₂–C₃ selectivity, with CH₄ conversion ranging from 20% to 30% at 800–900 °C^[21]. Thousands of catalysts have been explored, but no significant progress has been made. In 2017, Wang et al.^[22] developed a TiO₂-doped Mn₂O₃–Na₂WO₄/SiO₂ catalyst that exhibited excellent catalytic activity at low temperatures. At 720 °C, the CH₄ conversion reached 26%, with a C₂–C₃ selectivity of 76%. To date, this remains one of the few catalysts that demonstrate high catalytic activity in the OCM reaction. Guan et al.^[23] proposed a CO₂-assisted chemical-looping oxidative coupling of methane (CLOCM) method. Using an MnO–Na₂WO₄/SiO₂ catalyst at 750 °C, a CH₄ conversion of 14.29%, C₂–C₃ selectivity of 79%, and CO₂ conversion of 3.01% were achieved. It was confirmed that CO₂ could exchange oxygen with the oxygen vacancies on the catalyst surface, effectively replenishing lattice oxygen, maintaining a high concentration of active oxygen, inhibiting excessive oxidation of CH₄, and promoting the generation of C₂–C₃ hydrocarbons. Lu et al.^[24] constructed a Na₂WO₄–Mn₃O₄/m-SiO₂ nanoreactor, which achieved a CH₄ conversion of 39% and selectivity of 42.3% to C₂H₂ and C₂H₄ under plasma conditions. It was revealed that the hollow-mesoporous structure inhibited excessive dehydrogenation through the Debye shielding effect and enabled cascade catalysis involving Na₂WO₄ site dehydrogenation and Mn₃O₄ site coupling. Xie et al.^[25] developed a MnWO_x–NaWSiO_x dual-phase composite catalyst, which exhibited excellent catalytic performance in the OCM reaction. At 775 °C, the CH₄ conversion reached 32%, with a selectivity of 79% to C₂–C₃. It was revealed that the MnWO_x phase could efficiently activate O₂ to generate reactive oxygen species, which subsequently migrated to the surface of NaWSiO_x, thereby enabling a dual-phase synergistic promotion of the OCM reaction. This synergy not only improves the yield of C₂–C₃ hydrocarbons but also significantly lowers the

required reaction temperature and enhances catalytic stability, making the composite catalyst one of the most effective reported to date. Although extensive research has been conducted on the OCM reaction, reducing the reaction temperature while improving the selectivity and yield of target products remains a major challenge and research hotspot. Therefore, it is imperative to develop new methodologies for the OCM reaction.

In recent years, microwave-assisted reactions have attracted increasing attention for their remarkable capability to accelerate reaction rate and enhance selectivity under relatively mild conditions. Compared with conventional thermal heating, microwave irradiation not only accelerates the reaction rate but also effectively reduces overall energy consumption, thereby serving as an energy-efficient and sustainable heating approach^[26–28]. Studies have shown that microwave heating can significantly reduce energy consumption in OCM^[29–30]. Furthermore, Chen et al.^[31] and Roussy et al.^[32–33] demonstrated that microwave irradiation inhibits the deep oxidation of methyl radicals through rapid cooling, thereby improving the C₂ selectivity. Therefore, microwave heating can significantly enhance the OCM performance by improving temperature distribution and reaction path selectivity, which are crucial for the design and optimization of efficient microwave OCM catalysts.

Herein, we reported a novel method for OCM by microwave catalysis, for which a Mn₂O₃–TiO₂–Na₂WO₄/SiO₂+SiC microwave catalyst is developed via ball milling. This method can significantly reduce the reaction temperature while simultaneously enhance the product yield through the selective heating effect of microwaves, thereby enabling an efficient OCM reaction at a lower temperature. The effects of calcination treatment and reaction mode on the catalytic performance were systematically investigated by using the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), oxygen temperature-programmed desorption (O₂-TPD), and Raman characterization techniques. This study provides certain new insights for the design of efficient and stable OCM catalysts.

1 Experimental

1.1 Chemicals

Gas-phase silica (SiO₂, 250 m²/g) and manganese nitrate aqueous solution (Mn(NO₃)₂, 50%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Sodium tungstate dihydrate (Na₂WO₄·2H₂O, AR) was obtained from Tianjin Chemical Reagents Factory IV. Manganese trioxide (Mn₂O₃, AR) and titanium dioxide (TiO₂, AR) were supplied by Shanghai Aladdin Reagent Co., Ltd. Tetrabutyl titanate (C₁₆H₃₆O₄Ti, ≥98%) was purchased from Guoyao Group Chemical Reagents Co., Ltd. Deionized water (H₂O, secondary) was prepared in the laboratory. All chemicals were used as received, without further purification.

1.2 Catalyst preparation

The catalyst was prepared using the ball milling technique. Briefly, 3.875 g of SiO_2 , 0.561 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 0.31 g of Mn_2O_3 and 0.32 g of TiO_2 were mixed and placed into a ball milling tank. The mixture was milled for 2 h at a ball-to-material mass ratio of 10:1 and a rotation speed of 300 r/min. The catalyst composition, consisting of 6.2% Mn_2O_3 , 6.2% TiO_2 and 10% $\text{Na}_2\text{WO}_4/\text{SiO}_2$, was obtained and doped with SiC to prepare the microwave catalyst. One portion was directly used in the reaction, while the other was calcined at 800 °C for 5 h. For convenience, the catalyst is hereafter referred to $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2\text{+SiC}$. In the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2\text{+SiC}$ catalyst system, 1 g of $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2$ was physically mixed with 5 g of SiC. The activity data of SiC alone, showing its limited catalytic performance, is presented in Figure 2(a) and is further discussed in subsequent sections. SiC can effectively absorb microwave energy, thus improving the heating efficiency, but exhibits almost no catalytic activity in the temperature range of 550–750 °C.

1.3 Catalysts characterization

The XRD analysis was performed on a Rigaku D/MAX-2500/P X-ray polycrystalline powder diffractometer (Rigaku, Japan), with $\text{Cu K}\alpha$ as the radiation source, at a scanning range from 5° to 90°, a scanning speed of 10(°)/min, and a step size of 0.02°; the tube voltage and current were set to 40 kV and 250 mA, respectively. The XPS analysis was carried out on a Thermo Fisher Scientific ESCALAB 250 xi instrument (Thermo Fisher Scientific, USA), at approximately 2×10^{-7} mbar, with a monochromatic $\text{Al K}\alpha$ radiation source (1486.6 eV, 6 mA $\times$ 12 kV); the beam

spot size was 400 μm , using the CAE scanning mode. Raman spectroscopy was carried out on a Renishaw inVia Raman spectrometer (Renishaw, UK); a semiconductor laser was used as the excitation source, with a detection wavelength of 532 nm and the scanning range of 80–1000 cm^{-1} .

The O_2 -TPD test was carried out using an automatic chemical adsorption system. The samples were pretreated at 50 °C for 1 h under a He atmosphere (30 mL/min) and 50–100 mg of sample was placed in a reaction tube. The temperature was then increased to 500 °C at a rate of 10 °C/min, followed by drying and purging for 1 h. After cooling to 50 °C, an O_2 mixture (30 mL/min) was introduced for adsorption until saturation, and then the system was switched to a He atmosphere (30 mL/min) for purging for 1 h. Finally, the temperature was increased to 900 °C at 10 °C/min under a He atmosphere, and the desorbed gas was detected using a thermal conductivity detector (TCD).

1.4 Catalytic activity evaluation

The OCM reaction test was carried out using a vertical multi-atmosphere microwave catalytic reactor (Hunan Changyi Microwave Co., Ltd.). A schematic of the device is provided in Figure 1. A quartz tube was used as the reactor in the experiment. This reactor can quickly, efficiently and uniformly heat the absorbing materials and is commonly used in the gas-solid phase catalytic reactions. The catalyst was placed in a vertical tube and an improved thermocouple was positioned within the catalyst bed to minimize the interference from the microwave radiation. At each reaction temperature, the temperature fluctuation range was only 2–3 °C under steady state condition. The desired reaction temperature, such as 700 °C, is achieved by precisely regulating the microwave power output.

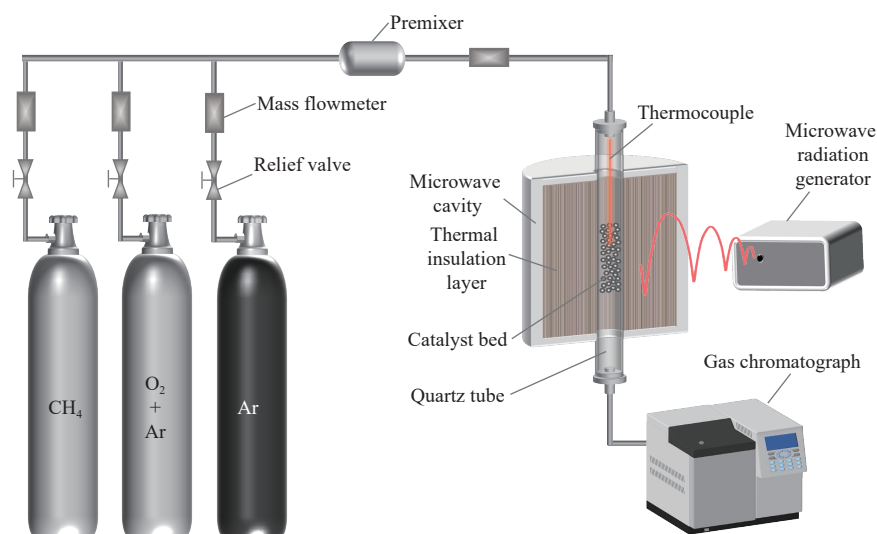


Fig. 1 Schematic diagram of the microwave catalytic reaction device

A microcomputer integrated in the microwave catalytic reactor is used to control the power output, thereby enabling precise regulation of the catalyst bed temperature. Conventional experiments for comparison were conducted in a tube furnace, with the catalyst placed in a horizontal quartz tube. During the evaluation, 1 g of catalyst (40–60 mesh) was mixed with 5 g of SiC and placed in a quartz reaction tube. The reaction atmosphere consisted of a mixture of CH₄, O₂ and Ar (CH₄:O₂:Ar = 5:1:4). The total space velocity was 8400 mL/(g·h) and the reaction temperature was monitored in real time using a thermocouple. The products were analyzed by gas chromatography (Agilent GC 7890A). H₂, O₂, CO and CO₂ were detected using a thermal conductivity detector (TCD) coupled with a TDX-01 packed column. CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ were analyzed using a hydrogen flame ionization detector (FID) coupled with a PoraPlot Q capillary column. The gas composition was quantified using the external standard method. By establishing the standard curves in advance, the content of each component in the exhaust gas was calculated using the fitted formula. Relevant data were collected after 10 min of reaction. For the catalyst characterization after the microwave reaction, SiC was first removed using a sieve to ensure that all analyzed samples were free of SiC.

The conversion of CH₄ (x_{CH_4}) and selectivity to C₂H₄, C₂H₆, C₃H₆, C₃H₈ ($s_{\text{C}_2-\text{C}_3}$) were calculated using the standard normalization method based on carbon atom conservation, following the formulae:

$$x_{\text{CH}_4} (\%) = \frac{\sum \text{converted reactants}}{\sum (\text{converted reactants}) + \sum (\text{remaining reactants})} \times 100\% \quad (1)$$

$$s_{\text{C}_2-\text{C}_3} (\%) = \frac{\text{moles of carbon atom in product N}}{\sum (\text{moles of carbon atom in reaction products})} \times 100\% \quad (2)$$

$$Y_{\text{C}_2-\text{C}_3} (\%) = x_{\text{CH}_4} \times s_{\text{C}_2-\text{C}_3} \times 100\% \quad (3)$$

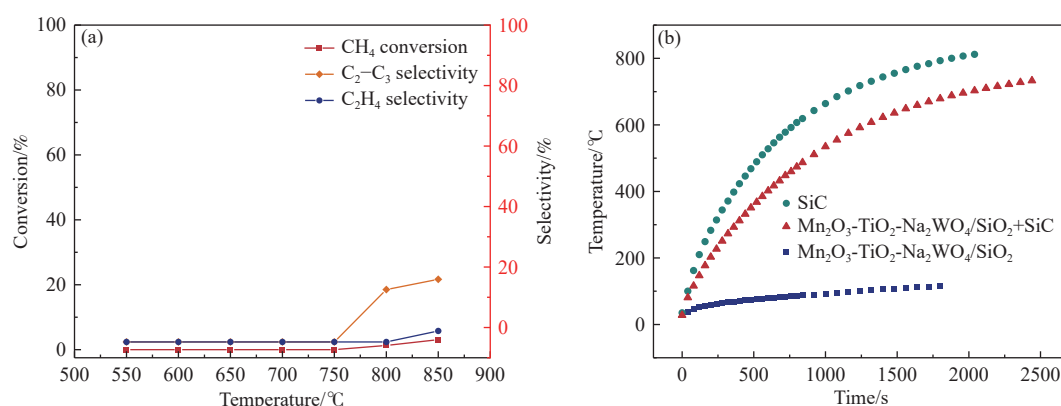
2 Results and discussion

2.1 Effect of SiC on the catalytic performance and microwave absorption

As the microwave catalytic reactor is not electrically heated, the desired temperature of catalyst bed is highly depended on the microwave absorbing properties of the catalyst bed materials themselves. To clarify the role of SiC in the reaction system, the OCM performance test was conducted separately, as shown in Figure 2(a). Apparently, SiC exhibits almost no catalytic activity in the temperature range of 550–750 °C, with only a very low conversion of approximately 2% at 800–850 °C, suggesting that SiC itself does not directly participate in the reaction below 750 °C. Further tests on the heating behavior of different catalysts shown in Figure 2(b) reveal that the equilibrium temperature of Mn₂O₃-TiO₂-Na₂WO₄/SiO₂ is only about 115 °C at 800 W microwave power; however, this temperature significantly increases to 760 °C when the catalyst is mixed with SiC and reaches 815 °C when SiC is used alone. That is, the introduction of SiC can significantly enhance the microwave absorption capacity of the catalyst bed, enabling the reaction bed to be heated up rapidly at a lower power microwave irradiation and providing the necessary temperatures for the OCM reaction.

2.2 Effect of calcination treatment on the catalyst performance

To investigate the effect of calcination treatment on the catalyst performance, the Mn₂O₃-TiO₂-Na₂WO₄/SiO₂ catalyst was calcined at 800 °C for 5 h in a muffle furnace and compared with the uncalcined counterpart. After adding SiC, their performances were further compared under microwave irradiation at different temperatures.



(a): Catalytic activity of SiC at different reaction temperatures; (b): Heating curves of different catalysts at a microwave power of 800 W.

Fig. 2 Catalytic activity and microwave absorption heating performance of SiC

As shown in Figure 3, the uncalcined catalyst displays pretty good performance at 700 °C, but the calcined counterpart is even better. At 700 °C, the uncalcined sample displays a CH₄ conversion of 24.2% and selectivity of 64.8% to C₂–C₃, with a C₂–C₃ yield of 14.5%. In contrast, the calcined counterpart achieves a CH₄ conversion of 26.6% and a selectivity of 76.5% to C₂–C₃, with a C₂–C₃ yield of 20.4%. Overall, the C₂–C₃ selectivity over the calcined catalyst can be stably maintained at approximately 75% across different reaction temperatures, which is significantly higher than those over the uncalcined sample. In addition, both catalysts show minimal variation in the activity within the temperature range of 700–800 °C, indicating that the temperature has a limited effect on the catalyst performance. This suggests that the calcination treatment is a key factor in enhancing the activity of the Mn₂O₃-TiO₂-Na₂WO₄/SiO₂ catalyst, which is further elucidated in the subsequent work.

2.3 Catalyst characterization

Figure 4 presents the XRD patterns of the Mn₂O₃-TiO₂-Na₂WO₄/SiO₂+SiC microwave catalyst before and after calcination and reaction. All samples exhibit α -cristobalite peaks at 21.8°, 26.6° and 32.0°, indicating that SiO₂ transforms into a stable phase at high temperature. Additionally, the characteristic peaks of Na₂WO₄ are observed near 24.0° and 29.0°, while the peaks of Mn₂O₃ appear at 28.3° and 33.0°^[34]. Notably, after calcination at 800 °C, a new diffraction peak emerges at 35.0°, which is attributed to MnTiO₃, while the intensity of the Mn₂O₃ peak is correspondingly weakened. This indicates that part of Mn₂O₃ reacts with TiO₂ to form the MnTiO₃ active phase, which is considered a key factor in promoting the conversion of CH₄ to C₂–C₃ in the OCM reaction^[22].

The surface element composition and valence state of the Mn₂O₃-TiO₂-Na₂WO₄/SiO₂+SiC catalysts were analyzed by XPS, as shown in Figure 5. The characteristic peaks of Na,

Mn, W, Ti, O and Si are observed throughout the spectrum, indicating that Mn₂O₃, TiO₂ and Na₂WO₄ have been successfully loaded onto the SiO₂ support. To further elucidate the role of the surface-active species in the catalyst, the O 1s and Mn 2p high-resolution spectra of the catalyst before and after calcination were fitted and analyzed.

Figure 5(b) shows that the O 1s spectrum can be decomposed into three peaks: 530.5 eV corresponding to the peroxy species O₂^{•−}; 532.4 eV to CO₃^{2−}; and 533.2 eV to the surface-adsorbed oxygen species O₂[−]^[35–37]. As shown in Table 1, the content of O₂^{•−} in the calcined sample is significantly higher than that in the uncalcined sample, which is consistent with their sequence in the OCM activity, indicating that O₂^{•−} plays a key role in the reaction. The higher the content of O₂^{•−}, the higher C₂–C₃ selectivity and yield the catalyst shows.

Figure 5(c) shows the high-resolution Mn 2p spectrum, which can be decomposed into two sub-bands: 2p_{3/2} and 2p_{1/2}. The peaks at 641.6 and 652.8 eV correspond to Mn³⁺, while those at 644.2 and 655.4 eV correspond to Mn⁴⁺^[38]. As shown in Table 1, the Mn⁴⁺/Mn³⁺ ratio for the uncalcined sample is 0.526, much higher than the value of 0.263 for the calcined sample, indicating the conversion of part Mn³⁺ to Mn⁴⁺ during the calcination process. It can be observed that the oxidation process of Mn³⁺ to Mn⁴⁺ readily induces lattice defects, enhances the surface oxygen migration ability, and improves the redox performance, thereby promoting the OCM reaction^[39]. Therefore, the high O₂^{•−} content and Mn⁴⁺/Mn³⁺ ratio are key factors that contribute to the excellent microwave reactivity of the Mn₂O₃-TiO₂-Na₂WO₄/SiO₂+SiC catalyst.

To explore the oxygen species on the catalyst surface, O₂-TPD tests were performed, as shown in Figure 6. The desorption peak below 300 °C corresponds to weakly physically adsorbed oxygen O_a^[40–41], which is not directly related to CH₄ conversion and is only detected in the O₂-TPD profiles of uncalcined catalyst.

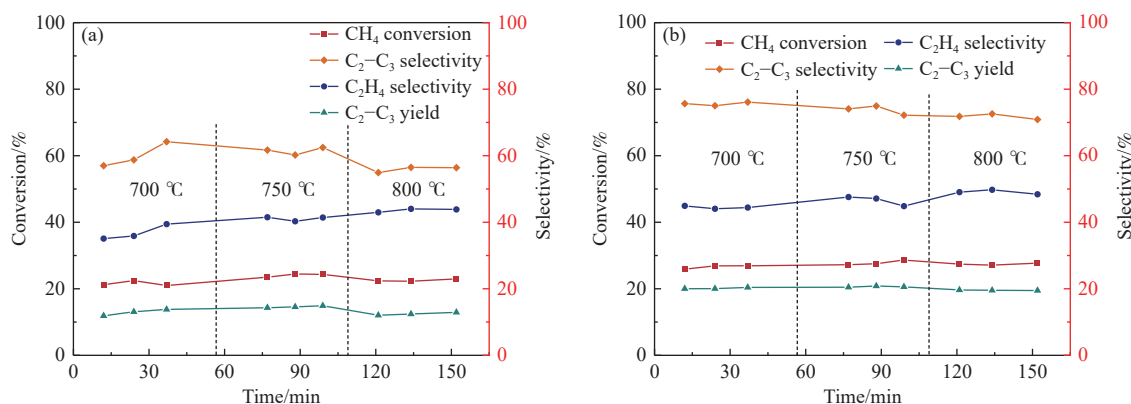


Fig. 3 Comparison in the activity under microwave catalytic reaction mode between the uncalcined catalyst (a) and calcined catalyst (b)

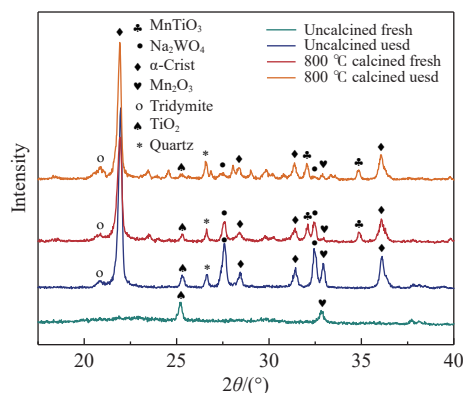
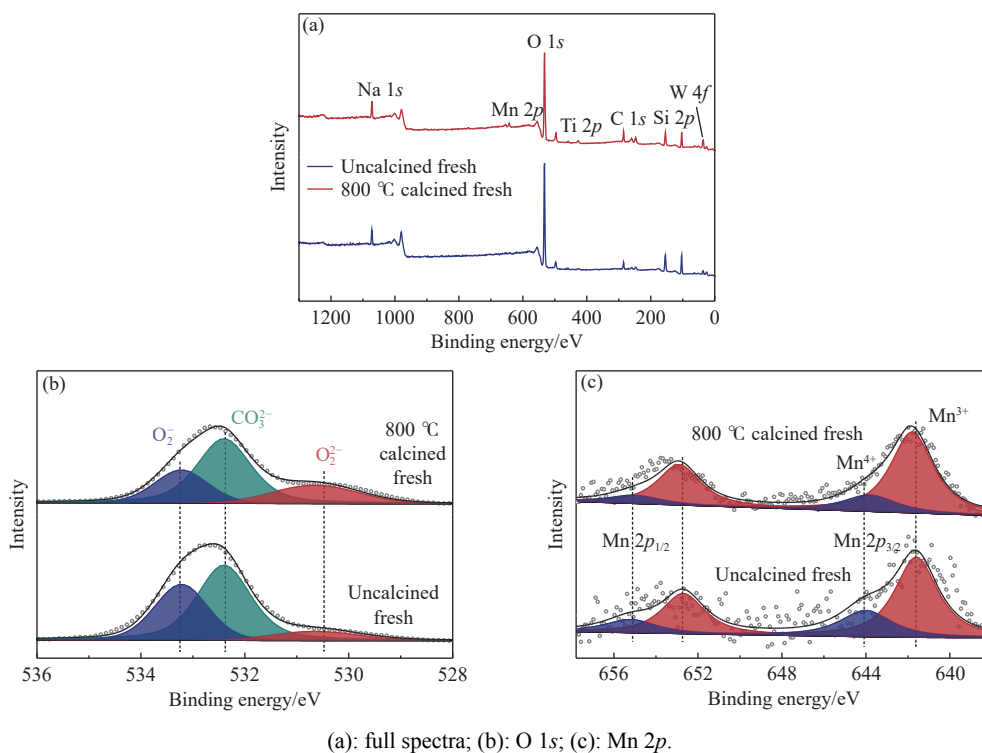


Fig. 4 XRD patterns of the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst before and after reaction

The desorption peak above 700 °C is attributed to the lattice oxygen species in Mn_2O_3 . The desorption peaks in the range of 300–700 °C are further divided into two regions: the peak at 300–450 °C corresponds to the surface reactive oxygen species O_β , which can activate CH_4 but is easily overoxidized to CO_2 at relatively low temperatures^[42];

in contrast, the peak at 450–700 °C is attributed to the surface lattice oxygen O_γ , which can effectively promote the conversion of CH_4 to C_2H_4 ^[41]. It is worth noting that the calcined catalyst exhibits distinct desorption peaks in the ranges of 450–700 °C and 750 °C, indicating the presence of more reactive oxygen species that can participate in the OCM reaction; accordingly, the overall catalytic performance of the calcined catalyst is improved.

Figure 7 presents the Raman spectra of the spent $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalysts after the reaction. Both calcined and uncalcined catalysts display the characteristic signal of MnTiO_3 after the reaction^[43], though the related signal of the calcined one is much stronger. Meanwhile, the Raman peak for Mn_2O_3 is not detected, indicating that Mn_2O_3 has been largely consumed during the reaction and converted to MnTiO_3 both in the bulk and on the surface of the catalyst. It can be confirmed that the formation of MnTiO_3 plays a crucial role in enhancing the performance of the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst in the OCM reaction.



(a): full spectra; (b): O 1s; (c): Mn 2p.

Fig. 5 XPS spectra of the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalysts

Table 1 XPS results of the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst before and after calcination treatment

Catalyst	Oxygen and manganese species		
	O_2^{2-}		$\text{Mn}^{4+}/\text{Mn}^{3+}$
	binding energy/eV	atomic fraction/%	
Uncalcined	530.7	14.08	0.526
800 °C calcined	530.5	21.36	0.263

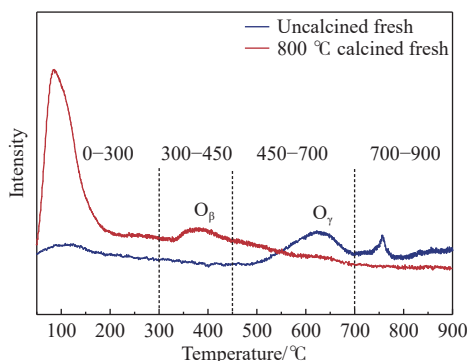


Fig. 6 O_2 -TPD profiles of the Mn_2O_3 - TiO_2 - Na_2WO_4 / SiO_2 + SiC catalysts

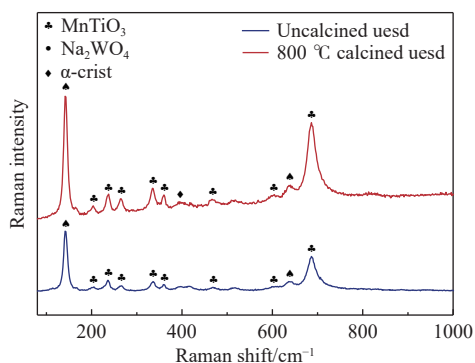


Fig. 7 Raman spectra of the spent Mn_2O_3 - TiO_2 - Na_2WO_4 / SiO_2 + SiC catalyst after the OCM reaction

2.4 Comparison in the catalytic performance between microwave and conventional reaction modes

To further investigate the effect of reaction mode on the catalyst activity in the OCM reaction, the calcined Mn_2O_3 - TiO_2 - Na_2WO_4 / SiO_2 + SiC catalyst was compared under both microwave and conventional conditions, as shown in Figure 8 and Table 2. At an initial temperature of 600 °C, both modes show insignificant activity. As the temperature increases, the catalyst activity is gradually improved, but the performance in microwave mode consistently outperforms that in the conventional mode. At 700 °C, the

CH_4 conversion, selectivity to C_2 - C_3 hydrocarbons and C_2 - C_3 yield in MCRM are 26.6%, 76.5% and 20.4%, respectively, much superior to the corresponding values of 12.3%, 61.9% and 7.5% under CRM. That is, the catalyst under MCRM exhibits higher CH_4 conversion and C_2 - C_3 selectivity, with its C_2 - C_3 yield nearly three times higher than that under conventional conditions. Combined with the characterization results, it can be observed that the calcination treatment promoted the interaction between Mn and Ti, leading to the formation of the active $MnTiO_3$ phase. In addition, the calcined catalyst displays a higher portion of O_γ species as measured by O_2 -TPD, which was beneficial to the formation of C_2 hydrocarbons, creating a synergistic effect with the enhanced activity in the microwave field. In summary, microwave heating not only significantly enhances catalyst activity at lower temperatures but also gives higher product yields under optimal reaction conditions. The microwave enables more uniform and efficient heating of the catalyst bed, which promotes the function of the active sites at lower temperatures. The rapid and selective microwave-matter interactions create a homogeneous reaction environment, reduce thermal gradients, and enhance catalyst stability. Consequently, the overall catalytic performance and product yield are significantly improved under microwave heating compared with the conventional heating that suffers from slow and uneven heat conduction^[44].

2.5 Stability evaluation of catalyst in microwave mode

To investigate the catalyst stability, the Mn_2O_3 - TiO_2 - Na_2WO_4 / SiO_2 + SiC microwave catalyst calcined at 800 °C was subjected to a continuous 20 h reaction test at 700 °C under microwave reaction mode. As shown in Figure 9, the catalyst maintains highly active even after prolonged reaction times. The CH_4 conversion and C_2 - C_3 selectivity remain stable at approximately 25% and 76%, respectively, while the C_2 - C_3 yield is maintained at around 20% without significant deactivation. That is, the Mn_2O_3 - TiO_2 - Na_2WO_4 / SiO_2 + SiC catalyst exhibits excellent stability and long-term application potential in the OCM reaction.

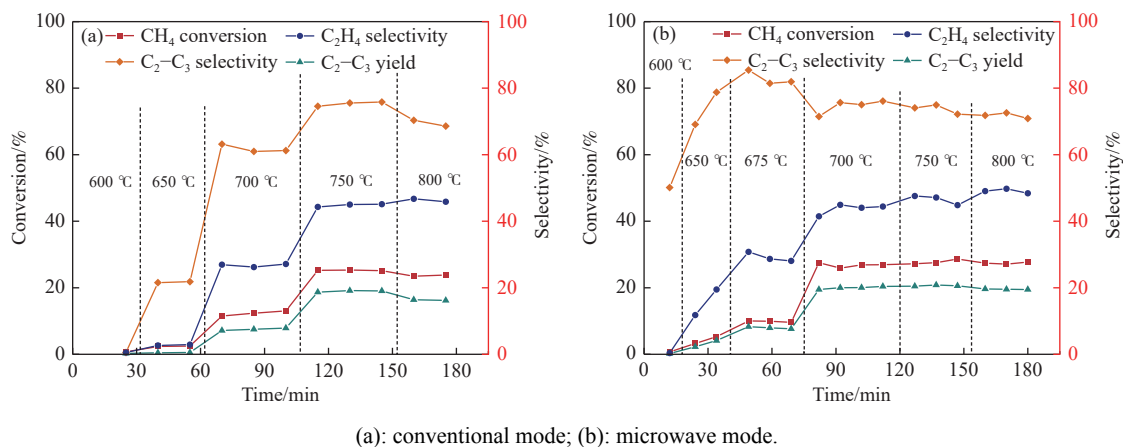
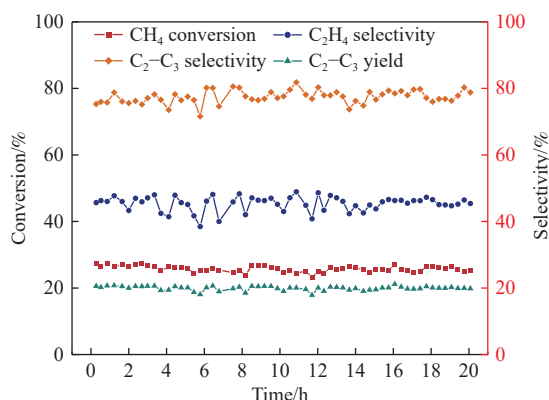
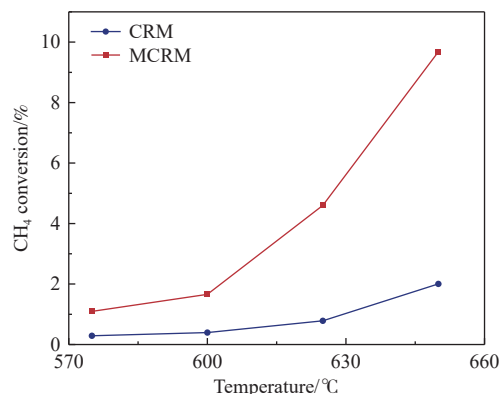


Fig. 8 Comparison of catalyst activity in the OCM reaction under different reaction modes

Table 2 Comparison in the performance of the calcined $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst between microwave and conventional modes

Model	CH_4 conversion/%	$\text{C}_2\text{-C}_3$ selectivity/%	C_2H_4 selectivity/%	$\text{C}_2\text{-C}_3$ yield/%
MCRM, 700 °C	26.6	76.5	44.5	20.4
CRM, 700 °C	12.3	61.9	26.7	7.5
MCRM, 750 °C	27.9	74.9	46.6	20.9
CRM, 750 °C	25	74.1	44.8	18.5
MCRM, 800 °C	27.5	72	49	19.8
CRM, 800 °C	23.5	69.6	46	16.3

Fig. 9 Stability test of the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst in the OCM reaction under MCRMFig. 10 Comparison of CH_4 conversion between MCRM and CRM

2.6 Microwave catalytic effect

2.6.1 Microwave direct catalytic effect

To investigate the effect of microwave irradiation on the kinetics and activation energy of the OCM reaction, the apparent activation energy was determined, with the CH_4 conversion rate in the temperature range of 575–650 °C over the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ microwave catalyst. By adjusting the inlet flow rate and catalyst loading, the methane conversion was maintained at a low level. As shown in Figure 10, the CH_4 conversion under MCRM is consistently higher than that under CRM, indicating that microwave irradiation benefits the OCM process and can lower the reaction temperature.

To consider the difference in OCM reaction kinetics between microwave and conventional reaction modes, the Arrhenius equation is used as follows:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where k is the rate constant, R is the molar gas constant, T is the thermodynamic temperature, E_a is the apparent activation energy, and A is the pre-exponential factor.

A linear regression fitting on $1/RT$ and $\ln(k)$ is made, as shown in Figure S1 of the Supporting Information and Table 3. The apparent activation energy of the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst in the conventional reaction mode is 173 kJ/mol, in good agreement with the value of approximately 192 kJ/mol reported in literature^[45]. In contrast, the apparent activation energy of the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst in the microwave reaction mode is decreased to 27.5 kJ/mol, indicating that microwave irradiation can significantly reduce the activation energy of OCM, thereby accelerating the reaction process.

2.6.2 Microwave selective catalytic effect

To further explore the effect of microwave irradiation on the product selectivity of the OCM reaction, the product distribution of the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ catalyst under different reaction modes was compared.

Table 3 Apparent activation energy for the oxidative coupling of methane

Mode	Catalyst	$E_a' / (\text{kJ} \cdot \text{mol}^{-1})$	Ref.
MCRM, 575–650 °C	$\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$	27.5	this work
CRM, 575–650 °C	$\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$	173	this work
CRM, 680–860 °C	$\text{NaWMn}/\text{SiO}_2$	192	[45]

The apparent activation energy (E_a') was calculated based on the Arrhenius equation.

As shown in Figure 11, the selectivity to C_2-C_3 and C_2H_4 under microwave conditions is higher than that under conventional mode, particularly in the temperature range of 650–700 °C, while the selectivity of both is similar at 750 °C. Meanwhile, the proportion of by-product CO_x in microwave mode is significantly reduced, with only 49.8% at 600 °C, much lower than the value of 100% observed in the conventional mode. These results indicate that microwave irradiation not only promotes the coupling reaction of methyl radicals but also effectively inhibits the deep oxidation process, thereby achieving a higher selectivity to the C_2-C_3 hydrocarbons.

The mechanism for the acceleration of chemical reactions by microwave irradiation remains a subject of debate. The traditional view is that microwave creates hot spots within the catalytic bed, with a temperature about 100–200 °C higher than the overall temperature, thereby accelerating the reaction rate^[46–47]. However, this study and other existing proofs demonstrate that, even if hot spots exist, the conversion and selectivity in the conventional reaction mode still do not reach the levels observed in the microwave reaction mode. Therefore, although the hot spot effect may contribute to the reaction under microwave irradiation in part, it is still insufficient to explain the enhanced performance under microwave conditions that significantly exceeds the thermodynamic predictions^[48].

An increasing number of studies support the selective catalytic effect of microwave irradiation. In the decomposition of H_2S , Chen et al.^[48–49] found that microwave irradiation can break the equilibrium limit and increase the conversion rate. Ramirez et al.^[27,50] demonstrated that microwave irradiation enables rapid selective heating of catalyst particles, while the gas phase maintains at a lower overall temperature, which helps to reduce the side reactions and improves the selectivity to the target product. These findings suggest that microwave irradiation not only heats up the system but also alters the reaction path and rate-determining steps by selectively coupling with polar or high-loss species.

Such an effect is particularly pronounced in the OCM system. The CH_4 conversion involves five parallel reactions,

as shown in Figure 12. CH_4 likely generates methyl radicals under the influence of surface-active oxygen, while C_2H_6 is possibly formed by coupling in the gas phase, which may be further converted into C_2H_4 . Simultaneously, the OH group likely facilitates the desorption of water and the regeneration of active sites. At a high temperature, some free radicals may react with gaseous O_2 or surface oxygen to form CO_x , which can potentially reduce the yield of the target product^[51–52]. Therefore, the reaction selectivity becomes a key factor limiting the efficiency of the OCM process. The selective catalytic effect of microwave irradiation is mainly reflected in two aspects. First, the promoting effect of microwave irradiation itself is selective and varies across different reaction systems^[44]. In the OCM reaction system, the promoting effect of microwave irradiation on side reactions is weaker than that on the main reaction, thereby the MCRM mode can greatly reduce the formation of by-products and improve the selectivity to target products. Second, microwave irradiation enables rapid heating of solid-phase particles, while the gas-phase temperature remains relatively lower, resulting in a gas-solid temperature difference^[27], which further suppresses the gas-phase chain reactions and surface deep oxidation. The results of Pak et al.^[53] also indicate that the complete oxidation of CH_4 occurs predominantly in the gas phase, whereas the oxidation of C_2H_4 mainly takes place on the catalyst surface, consistent with the findings of this study.

Further characterization results confirm the synergistic effect of $MnTiO_3-Na_2WO_4$ under microwave irradiation. The XRD and Raman results reveal the formation of $MnTiO_3$, while the XPS and O_2 -TPD results demonstrate that the catalyst is rich in active oxygen species capable of participating in the redox cycle. In addition, Na_2WO_4 inhibits side reactions and stabilizes the selectivity to target products. Under microwave irradiation, $MnTiO_3$ and Na_2WO_4 act synergistically, leading to simultaneous improvements in both activity and selectivity. Similarly, Kaneda et al.^[54] reported that a $SiC@MgO$ core-shell catalyst significantly enhanced the C_2 yield by improving the temperature distribution and avoiding hot spots and deep oxidation.

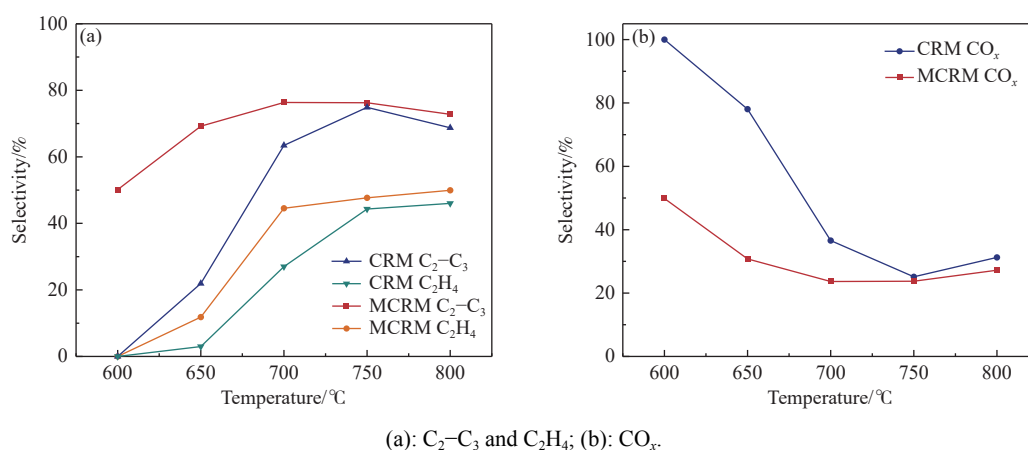


Fig. 11 Comparison of product selectivity in the OCM reaction over the $MnTiO_3-TiO_2-Na_2WO_4/SiO_2+SiC$ catalyst under different reaction modes

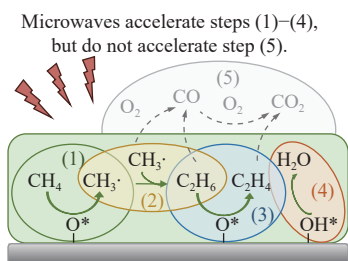


Fig. 12 Schematic diagram illustrating the possible reaction pathways of the OCM process under microwave irradiation

From a kinetic perspective, the apparent activation energy of the OCM reaction over the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2\text{+SiC}$ catalyst under MCRM is only 27.5 kJ/mol, much lower than the value of 173 kJ/mol under CRM that is consistent with the conventional value of approximately 200 kJ/mol reported in the literature. Similarly, in the decomposition of H_2S , the apparent activation energy over $\text{Mo}_2\text{C@CeO}_2$ decreased from 495.62 to 21.6 kJ/mol under microwave irradiation, suggesting the universality of microwave irradiation in significantly reducing the reaction energy barrier^[55]. Hunt et al.^[56] also found that the apparent activation energy dropped from 118.4 kJ/mol under conventional convective heating to 38.5 kJ/mol under microwave irradiation for the Boudouard reaction between carbon and carbon dioxide.

As a new type of heating method, microwave irradiation can significantly accelerate the reaction process and improve the reaction selectivity. In the reaction process, microwave irradiation plays two key roles. On the one hand, as an external field, microwave irradiation can regulate the reaction system and enhance reaction selectivity, often yielding better product selectivity than traditional thermocatalytic reactions. On the other hand, the energy provided by microwave irradiation not only heats the reaction system and increases the catalyst's temperature but also directly reduces the activation energy of the reaction, thereby accelerating the reaction process, which was also reported in one of our earlier works^[44]. Therefore, microwave radiation is not only an innovation of heating method, but also provides a new power source for reaction, which challenges the traditional heating method and has great application potential.

In summary, the promoting effect of microwave irradiation on the OCM process cannot be simply attributed to the hot spot effect but rather to the selective coupling among microwave, catalyst, and reactants. By rearranging the relative rates of the main and side reactions and regulating the gas-solid temperature field, microwave irradiation significantly reduces the activation energy and suppresses the formation of by-products. Combined with the synergistic effect of $\text{MnTiO}_3\text{-Na}_2\text{WO}_4$, it can be concluded that the selective catalytic effect of microwave irradiation is the key for the high-efficiency and low-temperature OCM reaction, which provides a new perspective for the future optimization and design of catalyst structures.

3 Conclusions

In this work, an $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2\text{+SiC}$ microwave catalyst was prepared using the ball-milling method and a new approach of microwave-catalytic OCM was proposed to achieve efficient conversion of methane to $\text{C}_2\text{-C}_3$ hydrocarbons at lower temperatures. The XRD, XPS, $\text{O}_2\text{-TPD}$ and Raman characterization results reveal that the calcination treatment can promote the interaction between Mn and Ti, increase the amount of peroxy species O_2^- and lattice oxygen O_γ , and thereby enhance both OCM reactivity and selectivity to target products. In addition, the calcined catalyst is superior to the uncalcined counterpart and MCRM is significantly better than CRM for the OCM reaction. For the OCM reaction at 700 °C in MCRM, the conversion of CH_4 , the selectivity to $\text{C}_2\text{-C}_3$ hydrocarbons, and the yield of $\text{C}_2\text{-C}_3$ are 26.6%, 76.5% and 20.4%, respectively, much superior to the values of 12.3%, 61.9% and 7.5% in CRM under identical reaction conditions. That is, the $\text{C}_2\text{-C}_3$ yield under microwave irradiation is about three times higher than that under the conventional mode. In addition, the $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2\text{+SiC}$ catalyst shows favorable stability at 700 °C during the OCM reaction in the MCRM for 20 h, with a methane conversion of above 25% and a selectivity of above 76% to $\text{C}_2\text{-C}_3$ hydrocarbons, with no evident deactivation observed. Further study illustrates that MnTiO_3 formation and microwave irradiation are the key to enhancing the OCM reactivity; the apparent activation energy under microwave irradiation is significantly reduced to 27.5 kJ/mol, compared with the value of 173 kJ/mol in the conventional mode. These results provide new insights into the development of efficient and stable OCM catalysts.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] LIAO D, YANG L, SONG G, et al. CO_2 -assisted oxidative dehydrogenation of ethane to ethylene over the ZnO-ZrO_2 catalyst[J]. J Fuel Chem Technol, 2023, 51(10): 1421–1431.
- [2] GUO X, FANG G, LI G, et al. Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen[J]. Science, 2014, 344(6184): 616–619.
- [3] CHEN R, WENG G. Sustainable energy resources for driving methane conversion[J]. Adv Energy Mater, 2023, 13(36): 2301734.
- [4] ZHANG Q, KANG J, WANG Y. Development of novel catalysts for Fischer-Tropsch synthesis: Tuning the product selectivity[J]. ChemCatChem, 2010, 2(9): 1030–1058.
- [5] KOSINOV N, HENSEN E J M. Reactivity, selectivity, and stability of zeolite-based catalysts for methane dehydroaromatization[J]. Adv Mater, 2020, 32(44): 2002565.

- [6] SONG S, SONG H, LI L, et al. A selective Au-ZnO/TiO₂ hybrid photocatalyst for oxidative coupling of methane to ethane with dioxygen[J]. Nat Catal, 2021, 4(12): 1032–1042.
- [7] LI Z, XIAO Y, CHOWDHURY P R, et al. Direct methane activation by atomically thin platinum nanolayers on two-dimensional metal carbides[J]. Nat Catal, 2021, 4(10): 882–891.
- [8] PETER M, MARKS T J. Platinum metal-free catalysts for selective soft oxidative methane→ethylene coupling. Scope and mechanistic observations[J]. J Am Chem Soc, 2015, 137(48): 15234–15240.
- [9] HAKI M, LINKE P, COSTA I M, et al. Methane conversion to aromatics via chemical synergy with OCM: Effect of periodic operation, temperature profile, and catalyst loading[J]. Fuel Process Technol, 2025, 270: 108189.
- [10] EFSTATHIOU A M, VERYKIOS X E. Transient methods in heterogeneous catalysis: Experimental features and application to study mechanistic aspects of the CH₄/O₂ (OCM), NH₃/O₂ and NO/He reactions[J]. Appl Catal A: Gen, 1997, 151(1): 109–166.
- [11] SOURAV S, FUSHIMI R R, WACHS I E. Current understanding of oxidative coupling of methane (OCM) reaction over supported Mn-Na₂WO₄ catalysts[J]. Catal Today, 2025: 115426.
- [12] SUN L, WANG Y, GUAN N, et al. Methane activation and utilization: Current status and future challenges[J]. Energy Technol, 2020, 8(8): 1900826.
- [13] TANG Y, LI Y, TAO F F. Activation and catalytic transformation of methane under mild conditions[J]. Chem Soc Rev, 2022, 51(1): 376–423.
- [14] ORTIZ-BRAVO C A, CHAGAS C A, TONIOLO F S. Oxidative coupling of methane (OCM): An overview of the challenges and opportunities for developing new technologies[J]. J Nat Gas Sci Eng, 2021, 96: 104254.
- [15] LUNSFORD J H. The catalytic oxidative coupling of methane[J]. Angew Chem Int Ed, 1995, 34(9): 970–980.
- [16] ZHAO K, GAO Y, WANG X, et al. Lithium carbonate-promoted mixed rare earth oxides as a generalized strategy for oxidative coupling of methane with exceptional yields[J]. Nat Commun, 2023, 14(1): 7749.
- [17] XIE Y, WANG W, CUI J, et al. K₂SO₄-promoted TiO₂ for the efficient oxidative coupling of methane[J]. Chem Eng Sci, 2024, 294: 120119.
- [18] ZAVYALOVA U, HOLENA M, SCHLÖGL R, et al. Statistical analysis of past catalytic data on oxidative methane coupling for new insights into the composition of high-performance catalysts[J]. ChemCatChem, 2011, 3(12): 1935–1947.
- [19] ARNDT S, LAUGEL G, LEVCHENKO S, et al. A critical assessment of Li/MgO-based catalysts for the oxidative coupling of methane[J]. Catal Rev, 2011, 53(4): 424–514.
- [20] FARRELL B L, IGENEGBAI V O, LINIC S. A viewpoint on direct methane conversion to ethane and ethylene using oxidative coupling on solid catalysts[J]. ACS Catal, 2016, 6(7): 4340–4346.
- [21] ARNDT S, OTREMB A T, SIMON U, et al. Mn-Na₂WO₄/SiO₂ as catalyst for the oxidative coupling of methane. What is really known[J]. Appl Catal A: Gen, 2012, 425: 53–61.
- [22] WANG P, ZHAO G, WANG Y, et al. MnTiO₃-driven low-temperature oxidative coupling of methane over TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst[J]. Sci Adv, 2017, 3(6): e1603180.
- [23] GUAN D, XIA S, GAO Y, et al. CO₂-assisted oxygen exchange to enhance the chemical looping oxidation coupling of methane[J]. ACS Sustainable Chem Eng, 2025, 13(19): 7166–7178.
- [24] LU C, WANG Y, TIAN D, et al. Shielded bifunctional nanoreactor enabled tandem catalysis for plasma methane coupling[J]. Nat Commun, 2025, 16(1): 4585.
- [25] XIE Y, CHENG J, WANG W, et al. Separation of MnWO_x and NaWSiO_x phases boosts oxidative coupling of methane[J]. Angew Chem Int Ed, 2025: e202503767.
- [26] BERMÚDEZ J M, BENEROSO D, REY-RAAP N, et al. Energy consumption estimation in the scaling-up of microwave heating processes[J]. Chem Eng Process: Process Intensif, 2015, 95: 1–8.
- [27] RAMIREZ A, HUESO J L, ABIÁN M, et al. Escaping undesired gas-phase chemistry: Microwave-driven selectivity enhancement in heterogeneous catalytic reactors[J]. Sci Adv, 2019, 5(3): eaau9000.
- [28] FIDALGO B, MENÉNDEZ J A. Study of energy consumption in a laboratory pilot plant for the microwave-assisted CO₂ reforming of CH₄[J]. Fuel Process Technol, 2012, 95: 55–61.
- [29] BOND G, MOYES R B, WHAN D A. Recent applications of microwave heating in catalysis[J]. Catal Today, 1993, 17(3): 427–437.
- [30] ZHANG X, LEE C S M, MINGOS D M P, et al. Oxidative coupling of methane using microwave dielectric heating[J]. Appl Catal A: Gen, 2003, 249(1): 151–164.
- [31] CHEN C, HONG P, DAI S, et al. Microwave effects on the oxidative coupling of methane over proton conductive catalysts[J]. J Chem Soc, Faraday Trans, 1995, 91(7): 1179–1180.
- [32] ROUSSY G, MARCHAL E, THIEBAUT J M, et al. C₂⁺ selectivity enhancement in oxidative coupling of methane over microwave-irradiated catalysts[J]. Fuel Process Technol, 1997, 50(2/3): 261–274.
- [33] ROUSSY G, THIEBAUT J M, SOUIRI M, et al. Controlled oxidation of methane doped catalysts irradiated by microwaves[J]. Catal Today, 1994, 21(2-3): 349–355.
- [34] CHUNTALAP Y, PANCHAN N, JUNSOMBOON J, et al. Effect of surface treatment technique on properties and performance of Na₂WO₄-TiO₂-MnO_x/SiO₂ for oxidative coupling of methane[J]. J Chem Technol Biot, 2021, 96(11): 3101–3113.
- [35] FERREIRA V J, TAVARES P, FIGUEIREDO J L, et al. Ce-doped La₂O₃ based catalyst for the oxidative coupling of methane[J]. Catal Commun, 2013, 42: 50–53.
- [36] GOPINATH C S, HEGDE S G, RAMASWAMY A V, et al. Photoemission studies of polymorphic CaCO₃ materials[J].

- Mater Res Bull, 2002, 37(7): 1323–1332.
- [37] JIANG T, SONG J, HUO M, et al. La_2O_3 catalysts with diverse spatial dimensionality for oxidative coupling of methane to produce ethylene and ethane[J]. RSC Adv, 2016, 6(41): 34872–34876.
- [38] LIU Y, DAI H, DENG J, et al. In situ poly (methyl methacrylate)-templating generation and excellent catalytic performance of $\text{MnO}_x/3\text{DOM LaMnO}_3$ for the combustion of toluene and methanol[J]. Appl Catal B: Environ, 2013, 140: 493–505.
- [39] GAO Y, WANG X, LIU J, et al. A molten carbonate shell modified perovskite redox catalyst for anaerobic oxidative dehydrogenation of ethane[J]. Sci Adv, 2020, 6(17): eaaz9339.
- [40] ZHANG C, GUO Y, GUO Y, et al. LaMnO_3 perovskite oxides prepared by different methods for catalytic oxidation of toluene[J]. Appl Catal B: Environ, 2014, 148: 490–498.
- [41] WEI Y, LIU J, ZHAO Z, et al. Highly active catalysts of gold nanoparticles supported on three-dimensionally ordered macroporous LaFeO_3 for soot oxidation[J]. Angew Chem Int Ed, 2011, 123(10): 2374–2377.
- [42] SUN W, GAO Y, ZHAO G, et al. $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4$ doping of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ enables increased activity and selectivity for low temperature oxidative coupling of methane[J]. J Catal, 2021, 400: 372–386.
- [43] JI S, XIAO T, LI S, et al. The relationship between the structure and the performance of Na-W-Mn/SiO_2 catalysts for the oxidative coupling of methane[J]. Appl Catal A: Gen, 2002, 225(1/2): 271–284.
- [44] ZHOU J, XU W, YOU Z, et al. A new type of power energy for accelerating chemical reactions: The nature of a microwave-driving force for accelerating chemical reactions[J]. Sci Rep, 2016, 6(1): 25149.
- [45] LOMONOSOV V I, GORDIENKO Y A, SINEV M Y. Kinetics of the oxidative coupling of methane in the presence of model catalysts[J]. Kinet Catal, 2013, 54(4): 451–462.
- [46] ZHANG X, HAYWARD D O, MINGOS D M P. Apparent equilibrium shifts and hot-spot formation for catalytic reactions induced by microwave dielectric heating[J]. Chem Commun, 1999, 11: 975–976.
- [47] HORIKOSHI S, SERPONE N. Role of microwaves in heterogeneous catalytic systems[J]. Catal Sci Technol, 2014, 4(5): 1197–1210.
- [48] CHEN J, XU W, ZHU J, et al. Highly effective direct decomposition of H_2S by microwave catalysis on core-shell $\text{Mo}_2\text{N-MoC@SiO}_2$ microwave catalyst[J]. Appl Catal B: Environ, 2020, 268: 118454.
- [49] XU W, WANG Q, PENG K, et al. Development of $\text{MgCo}_2\text{O}_4\text{-BaCO}_3$ composites as microwave catalysts for the highly effective direct decomposition of NO under excess O_2 at a low temperature[J]. Catal Sci Technol, 2019, 9(16): 4276–4285.
- [50] RAMIREZ A, HUESO J L, MALLADA R, et al. Microwave-activated structured reactors to maximize propylene selectivity in the oxidative dehydrogenation of propane[J]. Chem Eng J, 2020, 393: 124746.
- [51] DUDLEY G B, RICHERT R, STIEGMAN A E. On the existence of and mechanism for microwave-specific reaction rate enhancement[J]. Chem Sci, 2015, 6(4): 2144–2152.
- [52] SCHWACH P, HAMILTON N, EICHELBAUM M, et al. Structure sensitivity of the oxidative activation of methane over MgO model catalysts: II. Nature of active sites and reaction mechanism[J]. J Catal, 2015, 329: 574–587.
- [53] PAK S, QIU P, LUNSFORD J H. Elementary reactions in the oxidative coupling of methane over $\text{Mn/Na}_2\text{WO}_4/\text{SiO}_2$ and $\text{Mn/Na}_2\text{WO}_4/\text{MgO}$ catalysts[J]. J Catal, 1998, 179(1): 222–230.
- [54] KANEDA R, PALOMO J, HU L, et al. Oxidative coupling of methane under microwave: Core-shell catalysts for selective C_2 production and homogeneous temperature control[J]. Catal Sci Technol, 2023, 13(19): 5757–5766.
- [55] SUN H, CHEN J, TU C, et al. Robust microwave catalytic decomposition of H_2S into H_2 and S at low temperature over $\text{Mo}_2\text{C@CeO}_2$ catalysts[J]. J Fuel Chem Technol, 2025, 53(9): 1269–1282.
- [56] HUNT J, FERRARI A, LITA A, et al. Microwave-specific enhancement of the carbon-carbon dioxide (Boudouard) reaction[J]. J Phys Chem C, 2013, 117(51): 26871–26880.

$\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ 催化剂上微波催化 高效甲烷氧化偶联反应

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摘 要: 甲烷氧化偶联(OCM)是甲烷高值化利用的重要途径,但传统热催化反应过程存在转化率和选择性不足等问题。本工作提出微波催化 OCM 新方法,并研制了 $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ 微波催化剂。结果表明,经煅烧处理的 $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2+\text{SiC}$ 催化剂的性能优于未煅烧样品,且在微波催化反应模式(MCRM)下的催化性能显著优于常规反应模式(CRM)下。在 700 ℃, MCRM 模式下甲烷转化率为 26.6%, $\text{C}_2\text{-C}_3$ 烃类选择性为 76.5%, $\text{C}_2\text{-C}_3$ 收率为 20.4%。而在 CRM 模式下,甲烷转化率为 12.3%, $\text{C}_2\text{-C}_3$ 选择性为 61.9%, $\text{C}_2\text{-C}_3$ 收率仅为 7.5%。这说明 MCRM 能显著提高 $\text{C}_2\text{-C}_3$ 收率

至常规模式的约 3 倍, 表明微波不仅可以降低反应温度, 而且可以提高产物的收率。此外, 该 $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2\text{+SiC}$ 催化剂具有良好的稳定性, 在 700 °C 微波条件下连续进行 OCM 反应 20 h, 仍保持 25% 的甲烷转化率和 76% 的 $\text{C}_2\text{-C}_3$ 烃类选择性。进一步发现, 微波作用使催化剂表观活化能由常规模式下的 173 kJ/mol 显著降低至 27.5 kJ/mol, 通过选择性耦合促进自由基偶联并抑制深度氧化。这些结果为实现 CH_4 低温高效转化及绿色化工可持续发展提供了新思路。

关键词: 微波催化; 低温高效; $\text{Mn}_2\text{O}_3\text{-TiO}_2\text{-Na}_2\text{WO}_4/\text{SiO}_2\text{+SiC}$; 甲烷氧化偶联

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