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Research paper

TiO_2 -doped Mn_2O_3 - Na_2WO_4 / SiO_2 catalyst for oxidative coupling of methane: Solution combustion synthesis and $MnTiO_3$ -dependent low-temperature activity improvement

Pengwei Wang¹, Guofeng Zhao^{1,*}, Ye Liu, Yong Lu^{*}

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200062, China

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ABSTRACT

The Mn_2O_3 - Na_2WO_4 /SiO₂ catalyst is the most promising one among the enormous catalysts for the oxidative coupling of methane (OCM) but only at above 800 °C. No doubt that lowering temperature of the OCM process is at the forefront of this catalysis field. A promising low-temperature active and selective TiO₂-doped Mn_2O_3 , Na_2WO_4 /SiO₂ catalyst, consisting of 6 wt% TiO₂, 6 wt% Mn_2O_3 , 10 wt% Na_2WO_4 and SiO₂ in balance, is developed by solution combustion synthesis (SCS) method. This catalyst is capable of converting 20% CH₄ with 70% selectivity to C_2 - C_3 hydrocarbons even at 700 °C (catalyst bed temperature) and is stable for at least 250 h without deactivation sign, for a feed gas of 50% CH₄ in air using a gas hourly space velocity of 8000 mL g_{cat.}⁻¹ h⁻¹. In contrast, the non-TiO₂-doped SCS catalyst is almost inactive at 700 °C whereas it can achieve reactivity (~24% CH₄ conversion and ~74% C₂-C₃ selectivity) comparable to the TiO₂-doped one at 800 °C. XRD and Raman results evidently reveal that the formation of MnTiO₃ during the OCM process appears to be important for the low-temperature OCM activity improvement by TiO₂-doping.

1. Introduction

With the ever-growing resource and world output of natural gas and shale gas, methane conversion into the value-added chemicals and fuels has received more and more attentions from the worldwide petrochemical and energy industries, in order to alleviate our strong dependence on depleting oil resource [1,2]. Particularly, light olefins, the key building blocks in modern chemical industry, need an urgent production shift from oil to methane. Up to now, methane has been industrially converted into olefins in an indirect route, where methane is firstly and forcibly broken into the syngas (i.e., CO and H₂) through the catalytic steam or autothermal reforming at above 700 °C, followed by large-scaled conversion to methanol and then to olefins [3-5]. Additionally, syngas could also be directly converted into olefins in the presence of solid catalysts, such as the very recently reported bifunctional ZnCrO_x-SAPO catalyst [6] and the cobalt carbide nanoprisms [7] with outstanding selectivity under mild conditions. However, the syngas route is negatively energy-costing and such indirect manner causes low atom-utilization efficiency. Therefore, the direct methane conversion into olefins is highly desirable and a large number of researches have been dedicated for a couple of decays to achieving this

Corresponding authors.

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The oxidative coupling of methane (OCM) is considered to be a promising route to directly convert methane into C2-C3 hydrocarbon products in the presence of molecular oxygen. It has been well indicated from many studies that OCM is a sequential process combining the heterogeneous-catalysis and homogeneous-coupling to achieve the methane-to-olefins transformation [8-10]. The OCM catalysts aim to generate methyl radicals (CH3·) and avoid deep oxidation (i.e., to form CO, CO₂, and H₂O) over their surface [11,12]. Therefore, the most critical performance of OCM catalyst is able to generate selective surface oxygen radicals that act as the active sites for generating CH₃. [13–15]. Great attempts have been making to setup a catalyst recipe with such properties from the simple and complex oxides of alkaline, alkaline earth, and rare-earth elements [16-20]. Hundreds of catalysts have been examined aiming to favor C2-C3 selectivity and suppress overoxidation, such as the representative Li/MgO [21,22] and La-based oxides catalysts [23,24]. Li in Li/MgO catalyst acts as a structural modifier to enhance the catalyst OCM performance [21], but suffers from its loss during the long-term running [22]; the La-based catalysts suffer from the relatively lower C₂-C₃ selectivity. Among these catalysts, the Mn₂O₃-Na₂WO₄/SiO₂ is considered to be the most promising one, in





E-mail addresses: gfzhao@chem.ecnu.edu.cn (G. Zhao), ylu@chem.ecnu.edu.cn (Y. Lu).

¹ These authors contributed equally to this work.

terms of 20 ~ 30% methane conversion with 60 ~ 80% C₂-C₃ selectivity and in particular hundreds of hours stability [25]. However, this catalyst must be operated at above 800 °C and the slight reduction of temperature to below 800 °C will deteriorate sharply the catalyst activity even quench the OCM reaction [26].

In order to enhance the low-temperature performance of the Mn₂O₃-Na₂WO₄/SiO₂ catalyst, enormous work has been carried out on catalyst preparation and additive modification. The Mn₂O₃-Na₂WO₄/SiO₂ catalyst is usually prepared by the traditional methods such as incipient wetness impregnation, mixture slurry, and sol-gel methods [27]. Recently, solution combustion synthesis (SCS) strategy becomes more and more attractive to prepare homogeneous, high-purity, and complex nanostructured metal-oxides catalysts [28]. Compared to the traditional methods, SCS is a one-step method by self-propagating high-temperature synthesis with the raw materials mixed in liquid phase [29-31]. For example, the typical reaction between metal nitrate and glycine for the preparation of nanostructured La_2O_3 catalyst is shown by Eq. (1), where ϕ represents the fuel/oxidizer ratio: ϕ of 1 indicates the stoichiometric ratio that no more molecular oxygen is required; ϕ below 1 implies that molecular oxygen is generated; while ϕ above 1 means that molecular oxygen is needed [32]. Notably, modulating synthesis parameters such as fuel/oxidizer ratio and the property of fuels can tune the structure and texture of the as-synthesized catalyst [33,34]. Recently, the SCS method has been reported to be successfully applied to synthesize several promising OCM catalysts such as Sr-Al complex oxides, La2O3, La-Sr-Al complex oxides, and Mn2O3-Na2WO4/SiO2 [35], with improved C2-C3 yield. In particular, the SCS-prepared Mn2O3-Na2WO4/ SiO₂ catalyst successfully reduces the reaction temperature from above 800 °C for the regularly-prepared counterparts to 750 °C along with high C₂-C₃ yield of ca. 25% (for a feed gas of CH₄:O₂:N₂ = 2:1:0.63). In addition, Ce and La can also be easily introduced into the Mn₂O₃-Na₂WO₄/SiO₂ catalyst by SCS method [35,36], which generates more reactive oxygen to further enhance the catalyst performance.

$$2\text{La}(\text{NO}_3)_3 + 3.33\phi\text{H}_2\text{N}(\text{CH}_2)\text{CO}_2\text{H} + 7.5(\phi - 1)\text{O}_2 \rightarrow$$
$$\text{La}_2\text{O}_3 + \phi(6.67\text{CO}_2 + 8.33\text{H}_2\text{O} + 1.67\text{N}_2) + 3\text{N}_2$$
(1)

Besides opening up new preparation method, additive modification is another aspect to promote the catalyst low-temperature performance [37–39]. As mentioned above, activating oxygen molecules into desirable reactive oxygen species on the catalyst surface is a critical step that induces the methane activation to produce CH₃· and then C₂-C₃ products. Freund et al. [37] reported a highly ordered CaO film modified with Mo²⁺, and supposed that the generated superoxide anions (O₂⁻) attributes to methane activation. Trunschke et al. [38] provided the Fe and Cu co-doped polycrystalline MgO, which can effectively activate oxygen to produce peroxy (O₂²⁻) species for promoting the ethane or ethylene formation. Therefore, a question jumping out is whether the OCM reaction temperature is dominated by the O₂ activation temperature. If so, making efforts to lower the O₂ activation temperature by additive modification seems to be another key to improving the lowtemperature activity for the Mn₂O₃-Na₂WO₄/SiO₂ catalyst.

In this paper, we present a strategy to introduce TiO₂ into the Mn_2O_3 - Na_2WO_4/SiO_2 catalyst by SCS method to prepare TiO₂-doped counterpart, with the aim to enhance the low-temperature catalytic activity and selectivity for the OCM process. The catalyst preparation parameters (including Ti-precursors, fuel/oxidizer ratio, calcination temperature, and active component loadings) and OCM reaction conditions (including CH₄/O₂ molar ratio, gas hourly space velocity (GHSV), and reaction temperature) were systematically investigated. Excitingly, the reaction temperature (the real catalyst bed temperature in present work) could be reduced from > 800 °C for the regular literature Mn_2O_3 - Na_2WO_4/SiO_2 catalyst to 700 °C after TiO₂-doping through the SCS method, achieving 20% CH₄ conversion with 70% selectivity to C₂-C₃. Probings of catalyst phase and surface, using XRD and Raman, reveal that the in-situ formation of MnTiO₃ is paramount

for the enhancement of catalyst low-temperature activity for the OCM process.

2. Experimental

2.1. Materials

All chemicals in this work were purchased from Sinopharm Chemical Reagent Co., Ltd, China: sodium tungstate dihydrate (AR), 50 wt% manganese(II) nitrate aqueous solution (AR), tetraethyl orthosilicate (AR), tetrabutyl titanate (CP), titanium isopropoxide (CP), titanium *n*-propoxide (CP), and 65 wt% nitric acid aqueous solution (AR). They were all used as received.

2.2. Catalyst preparation

Regular Mn₂O₃-Na₂WO₄/SiO₂ catalyst and the TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst were prepared by the reported SCS method [35,36]. Mn(NO₃)₂ aqueous solution and Na₂WO₄ were employed as precursors for Mn-, Na- and W-containing components. Tetraethyl orthosilicate and titanate (titanium isopropoxide, titanium n-propoxide or tetrabutyl titanate) were the precursors for SiO₂ and TiO₂ compounds while serving as fuels in the SCS process. For the SCS method, HNO3 was used as oxidizer. The ϕ (i.e., fuel/oxidizer ratio) was tuned in the range from 1 to 3 by adding appropriate amount of 65 wt% HNO3 aqueous solution. In brief, the Mn, Na, and W precursors were mixed together with the tetraethyl orthosilicate and titanate in deionized water in a ceramic bowl, and appropriate amount of HNO₃ according to the ϕ vale was added subsequently. The mixture was then continuously stirred at 80 °C until it was transformed into the sticky gel. Subsequently, the ceramic bowl with such gel was transferred into a muffle furnace. When heating the gel to 300 °C, self-ignition combustion took place to form brown solid product. A stainless steel screen with 140 mesh opening was used for covering the ceramic bowl to prevent the formed powders from escaping. All as-synthesized catalysts were calcined at 500-900 °C in air for 4 h, crashed and sieved to collect 100-120 mesh fine particles for use in OCM reaction testing. The catalyst was denoted as a-TiO₂-b-Mn₂O₃-c-Na₂WO₄/SiO₂- ϕ -x (a, TiO₂ loading; b, Mn_2O_3 loading; c, Na_2WO_4 loading; ϕ , fuel/oxidizer ratio; x, calcination temperature).

2.3. Catalyst characterization

Catalysts were characterized by X-ray diffraction (XRD, Rigaku Uitima IV diffractometer with Cu K α radiation (35 kV and 25 mA); Japan), scanning electron microscopy (SEM, Hitachi S-4800; Japan) equipped with an energy dispersive X-Ray fluorescence spectrometer (EDX, Oxford; UK) and inductively coupled plasma atomic emission spectrometry (ICP-AES, ICP Thermo IRIS Intrepid II XSP; USA). Specific surface area (SSA) was determined from N₂ adsorption isotherm at -196 °C using standard Brunauer-Emmett-Teller (BET) theory on a Quanta chrome Autosorb–3 B instrument (USA). Raman measurements were carried out using a Raman spectrometer (Renishaw inVia) with a 532 nm semiconductor laser as excitation and the samples were scanned from 800 to 2000 cm⁻¹. It is equipped with a charge coupled device (CCD) camera enabling microanalysis on a sample point.

2.4. Reactivity tests

OCM reaction was performed in a fixed-bed quartz tube reactor (400 mm length and 16 mm inner diameter straight cylindrical tube) under atmospheric pressure. The catalyst of 1.0 g was loaded in the reactor and the catalyst bed thickness was approximately 10 mm in each OCM reaction testing. The reactants, methane (99.99%), oxygen (99.999%), and nitrogen (99.99%) as dilution, were co-fed into the reactor by three calibrated mass flow controllers. GHSV was varied in



Fig. 1. SEM images of typical SCS-synthesized TiO₂doped catalyst before (A) and after (B) calcining at 800 °C; (C) XRD pattern of calcined TiO₂-doped catalyst; (D) Raman spectra: (a) the calcined TiO₂doped catalyst, (b) Mn₂O₃, (c) TiO₂, (d) Na₂WO₄. Note of SCS preparation: titanium isopropoxide (Ti-I) as Ti precursor, ϕ of 2, and calcination temperature of 800 °C; 6 wt% TiO₂, 6 wt% Mn₂O₃ and 10 wt% Na₂WO₄ in catalyst.

the range of 2000–15000 mL g_{cat.}⁻¹ h⁻¹ and CH₄:O₂ molar ratio was investigated from 2 to 8. In our present work, reaction temperature is the catalyst bed temperature, which was monitored by a thermo-couple placed in the middle of the catalyst bed. The catalysts were activated by directly undergoing the OCM reaction at 800 °C for 2 h. After that, the catalyst bed reaction temperature was gradually reduced to 780, 760, 720, and 700 °C, to investigate their temperature-dependent OCM performance. All data were collected after reaction at each temperature for at least 0.5 h (ensure to reach steady-state). The effluent gas was analysed with an online gas chromatograph equipped with a thermal conductivity detector (TCD), using a 30 m DM-Plot Q capillary column (for the separation of CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, and C₃H₈) and a 60 m DM-Plot Msieve 5A column (for the separation of N₂, O₂, CO, and CH₄) in parallel.

3. Results and discussion

3.1. Catalyst characteristics

Fig. 1 and Table 1 show the characteristics of catalysts in terms of surface morphology, chemical composition, and textural and structural properties. Fig. 1A shows the SEM image of the typical as-synthesized TiO_2 -doped Mn_2O_3 - Na_2WO_4/SiO_2 catalyst by SCS method. It can be seen that the catalyst surface is rough and porous, which is the characteristic of sample prepared by SCS method [28]. After calcining at 800 °C, the rough surface become smooth associated with serious pore

Table 1 SSA and real contents of Mn, W, Na, and Ti of the calcined catalysts.

Catalyst	SSA (m ² /g)	Pore Size (nm)	Content ^a (wt%)			
			Mn	w	Na	Ti
TiO ₂ -Mn ₂ O ₃ -Na ₂ WO ₄ /SiO ₂ Mn ₂ O ₃ -Na ₂ WO ₄ /SiO ₂	1.6 1.4	24.8 23.2	4.0 3.9	5.2 4.9	1.1 1.0	3.5 0.0

^a All contents were determined by AES-ICP measurements.

collapse, being consistent with its small specific surface area (SSA) of $1.4 \text{ m}^2 \text{ g}^{-1}$ (Fig. 1B, Table 1). Contents of Mn, W and Na in our TiO₂doped Mn₂O₃-Na₂WO₄/SiO₂ catalysts by SCS method are almost identical to those of the regular Mn₂O₃-Na₂WO₄/SiO₂ catalyst while both of them show similar small SSA (1.2-1.4 $m^2 g^{-1}$) (Table 1). Fig. 1C shows the XRD patterns of the as-calcined TiO₂-doped catalyst. The phases of a-cristobalite, Na₂WO₄ and Mn₂O₃ are clearly observed, which are critical for the regular Mn₂O₃-Na₂WO₄/SiO₂ catalyst. What to be noted is that Mn²⁺ (from the Mn(NO₃)₂ precursor) is fully oxidized into Mn³⁺ because of the sufficient oxygen in the calcining environment, while the introduced Ti element is transformed into TiO2. The as-calcined catalyst was also characterized by Raman spectroscopy as well as the pure samples of Na₂WO₄, TiO₂ and Mn₂O₃ for reference. Clearly, the ascalcined catalyst shows a very strong Mn₂O₃ Raman band compared to the bands to TiO₂ and Na₂WO₄ (Fig. 1D). In combining this information with the fact that Mn₂O₃ shows the weaker XRD peak than TiO₂ and Na₂WO₄, it is rational to infer that the Mn₂O₃ dominates the catalyst surface.

3.2. Catalytic OCM performance of TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst

3.2.1. Effects of Ti precursors, ϕ , and calcination temperature

As well known, the SCS preparation parameters including Ti precursors, ϕ , and calcination temperature, always play critical roles in tuning the catalyst performance [28]. The effect of Ti-precursors was studied on the OCM performance of our SCS catalysts, by employing the common isopropoxide (denoted as Ti-I), titanium *n*-propoxide (denoted as Ti-II), and tetrabutyl titanate (denoted as Ti-III). By setting TiO₂, Mn₂O₃, and Na₂WO₄ loadings as 6, 6, and 10 wt%, ϕ as 2, and calcination temperature as 800 °C, three catalysts were obtained by SCS method and denoted as TiO₂-I-Mn₂O₃-Na₂WO₄/SiO₂, TiO₂-II-Mn₂O₃-Na₂WO₄/SiO₂, and TiO₂-III-Mn₂O₃-Na₂WO₄/SiO₂. These catalysts were tested in the OCM reaction at 700 °C for a feed gas of CH₄:O₂:N₂ = 5:1:4, using a total GHSV of 8000 mL g_{cat.}⁻¹ h⁻¹, with the results as shown in Fig. 2A. Prior to testing experiments at 700 °C,



Fig. 2. Effects of (A) Ti precursor, (B) fuel/oxidizer ratio, and (C) calcination temperature on the catalytic OCM performance of the Ti-doped Mn_2O_3 - Na_2WO_4/SiO_2 catalyst. Reaction conditions: 1.0 g catalyst, 700 °C, GHSV of 8000 mL g_{cat} ⁻¹ h⁻¹, CH₄/ O_2/N_2 molar ratio of 5/1/4, atmospheric pressure. Note of catalyst activation: by undergoing OCM reaction at 800 °C for 2 h.

the catalysts were in situ activated by undergoing the OCM reaction at 800 °C for 2 h. Clearly, the TiO₂-I-Mn₂O₃-Na₂WO₄/SiO₂ catalyst achieves higher activity and selectivity compared to the TiO₂-II-Mn₂O₃-Na₂WO₄/SiO₂ and TiO₂-III-Mn₂O₃-Na₂WO₄/SiO₂. Over the TiO₂-I-Mn₂O₃-Na₂WO₄/SiO₂ catalyst, a high CH₄ conversion of 20% is obtained with a high C₂-C₃ selectivity of 70%. Therefore, titanium isopropoxide (Ti-I) is selected to prepare the OCM catalysts by SCS method for follow-up studies.

In addition, ϕ is another important parameter for the SCS catalysts. Its effect on the TiO₂-I-Mn₂O₃-Na₂WO₄/SiO₂ catalyst was investigated in a range from 1 to 3 (i.e., $\phi = 1.0, 1.5, 2.0, 2.5, \text{ and } 3.0$, respectively) with the results as shown in Fig. 2B. At 700 °C and a GHSV of 8000 mL g_{cat.}⁻¹ h⁻¹, CH₄ conversion and C₂-C₃ selectivity are improved from 14 to 20% and from 65 to 70% along with the increase of ϕ from 1.0 to 2.0, and then reaches a plateau with further increasing ϕ up to 3.0. Accordingly, the optimal value of ϕ is determined as 2.0.

Moreover, the effect of calcination temperature was also studied on the OCM performance of the TiO₂-I-Mn₂O₃-Na₂WO₄/SiO₂ catalyst by fixing ϕ to 2.0. As shown in Fig. 2C, in the calcination temperature range studied from 500 to 900 °C, a volcano-shaped CH₄ conversion evolution is observed with a maxima of 20% at a calcination temperature of 800 °C; while C₂-C₃ selectivity is increased from 66 to 70% with calcination temperature from 500 to 800 °C but shows no alteration with further increasing the calcination temperature to 900 °C. Clearly, the optimal calcination temperature is found to be 800 °C for achieving a good SCS catalyst using titanium isopropoxide (Ti-I) as precursor at a ϕ of 2.0.

3.2.2. Effects of TiO₂, Mn₂O₃, and Na₂WO₄ loadings

Effects of TiO₂, Mn₂O₃, and Na₂WO₄ loadings on the TiO₂-I-Mn₂O₃-Na₂WO₄/SiO₂ catalyst performance were systematically investigated at a GHSV of 8000 mL g_{cat}⁻¹ h⁻¹ for a feed gas of CH₄:O₂:N₂ = 5:1:4. What to be first noted is that Mn and Ti species could be combined and transformed into MnTiO₃ in the real reaction stream, which is paramount for the improvement of low-temperature OCM activity of catalysts (detailed results and discussion given in the posterior sections of 3.4 and 3.5). The Mn:Ti ratios of 1:1.5, 1:2, 1.5:1 and 2:1 were also tested (Fig. S2). The results show that the catalytic performance with these Mn:Ti ratios is similar to that with Mn:Ti ratio of 1:1 (Fig. 3A), indicating that the catalyst performance is mainly determined by MnTiO₃ rather than the excessively-formed TiO₂ (for the catalysts with Mn:Ti ratios of 1:1.5 and 1:2) or Mn₂O₃ (for the catalysts with Mn:Ti ratios of 1.5:1 and 2:1). Therefore, the loading of TiO₂ plus Mn₂O₃ at a fixed Ti/Mn molar ratio of 1:1 was initially investigated



from 4 to 20 wt% with a constant Na₂WO₄ loading of 10 wt%. CH₄ conversion and C₂-C₃ selectivity against the loading of TiO₂ plus Mn₂O₃ are shown in Fig. 3A. At 700 °C, clearly, the CH₄ conversion and C₂-C₃ selectivity are promoted from 15 to 20% and 55–70%, along with the increase in the loading of TiO₂ plus Mn₂O₃ from 4 to 12 wt%. Nevertheless, further increasing the loading of TiO₂ plus Mn₂O₃ to 20 wt% does not yield better CH₄ conversion as well as C₂-C₃ selectivity. Subsequently, effect of Na₂WO₄ loading (from 5 to 20 wt%) was investigated on the TiO₂-I-Mn₂O₃-Na₂WO₄/SiO₂ catalyst performance. To address this issue, the loading of TiO₂ plus Mn₂O₃ was fixed at 12 wt%. As seen in Fig. 3B, the CH₄ conversion and C₂-C₃ selectivity are slightly increased from 18 to 20% and 68–70% with increasing the Na₂WO₄ loading from 5 to 10 wt%, and then plateau with further increasing the Na₂WO₄ loading up to 20 wt%.

Based on the above systematic investigation and analysis, the catalyst preparation conditions can be optimized as following: titanium isopropoxide (Ti-1) as Ti precursor, ϕ of 2, TiO₂ plus Mn₂O₃ loading of 12 wt% with Mn/Ti molar ratio of 1:1 (i.e., 6 wt% Mn₂O₃ and 6 wt% TiO₂), Na₂WO₄ loading of 10 wt%, and calcination temperature of 800 °C. This promising catalyst is denoted as 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800.

3.2.3. Effects of reaction variables

Fig. 4 shows the effect of reaction variables on the OCM performance over the 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800 catalyst. Clearly, the CH₄ conversion and C₂-C₃ selectivity are dependent on the CH₄/O₂ molar ratio, GHSV, and catalyst bed temperature. The CH₄/O₂ molar ratio is very critical to the CH₄ conversion and especially the selectivity to C₂-C₃ products. As shown in Fig. 4A, use of low CH₄/O₂ molar ratio (i.e., high oxygen concentration in catalyst bed) results in a reduction of selectivity due to the facilitation of deep oxidation, whereas the high CH₄/O₂ molar ratio (i.e., low oxygen concentration) worsens the CH₄ conversion other than the selectivity. Such observation is in accordance with the reported results [40]. At 700 °C and a GHSV of 8000 mL $g_{cat.}^{-1}$ h⁻¹, the CH₄ conversion is monotonously decreased from 26.5 to 15.8% while the C_2 - C_3 selectivity is inversely from 52.5 to 76.5% with the increase in CH_4/O_2 molar ratio from 2 to 8 (Fig. 4A). A volcano-shaped yield to $C_2\mathchar`-C_3$ is observed against the CH_4/O_2 molar ratio and a C2-C3 yield maxima of 14% appears at the CH4/O2 molar ratio of 5. In this case, the CH₄ conversion of 20% is achieved with a high C₂-C₃ selectivity of 70%.

Fig. 4B shows the GHSV dependent CH_4 conversion and C_2 - C_3 selectivity for a feed gas with CH_4/O_2 molar ratio of 5 at 700 °C. With the increase in the GHSV from 2000 to 8000 mL $g_{cat.}^{-1}$ h⁻¹, clearly, the

Fig. 3. Effects of the loadings of (A) TiO₂ plus Mn_2O_3 and (B) Na_2WO_4 on the catalytic OCM performance of the TiO₂-I- Mn_2O_3 - Na_2WO_4 /SiO₂-2-800 catalyst. Reaction conditions: 1.0 g catalyst, 700 °C, GHSV of 8000 mL g_{cat.}⁻¹ h⁻¹, CH₄/ O_2/N_2 molar ratio of 5/1/4, atmospheric pressure. Note of catalyst activation: see that in Fig. 2.



Fig. 4. CH₄ conversion and C₂-C₃ selectivity for the OCM reaction against (A) CH₄/O₂ ratio at GHSV of 8000 mL g_{cat.}⁻¹ h⁻¹ and (B) GHSV for feed gas of CH₄/O₂/N₂ = 5/1/4, using 6-TiO₂-1-6-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800 catalyst. Reaction temperature (i.e., catalyst bed temperature) dependent CH₄ conversion and C₂-C₃ selectivity for the OCM reaction for feed gas of CH₄/O₂/N₂ = 5/1/4 at GHSV of 8000 mL g_{cat.}⁻¹ h⁻¹, using (C) 6-TiO₂-1-6-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800 and (D) 6-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800 and (D) 6-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800 at lyst. Note of catalyst activation: see that in Fig. 2.

CH₄ conversion is decreased slightly from 24.8 to 20% whereas the selectivity to C₂-C₃ is inversely increased from 55 to 70% dramatically. With further increasing the GHSV up to 15000 mL g_{cat.}⁻¹ h⁻¹, the CH₄ conversion shows a big reduction to 12.8% and the selectivity to C₂-C₃ is improved further but slowly to 74.8%. Similar observation is consistent with the literature report [41].

Fig. 4C shows the CH₄ conversion and C₂-C₃ selectivity against the reaction temperature using a feed gas of $CH_4:O_2:N_2 = 5:1:4$ at a GHSV of 8000 mL $g_{cat.}^{-1} h^{-1}$, showing that high temperature is favourable to improve not only the CH₄ conversion but also the C₂-C₃ selectivity. At a high temperature of 800 °C, a high CH₄ conversion of 25% is achievable with a high C₂-C₃ selectivity to 74%. Most notably, the CH₄ conversion and C2-C3 selectivity at this level (i.e. $\sim\!20\%$ conversion and $\sim\!70\%$ selectivity) is well sustained after decreasing the catalyst bed temperature to 700 °C. Even at 680 °C, an interesting CH₄ conversion of 14% can still be achieved with a fair C2-C3 selectivity of 55%. For comparison, the non-TiO₂-doped Mn_2O_3 -6-Na₂WO₄-10/SiO₂ (6 wt% Mn₂O₃ and 10 wt% Na₂WO₄ and without TiO₂-doping) catalyst was also prepared by SCS method [35,36] under the optimum preparation conditions, and was examined in the OCM reaction under the identical reaction conditions. As shown in Fig. 4D, not surprisingly, this reference catalyst achieves a high CH₄ conversion of 24% with a nice C₂-C₃ selectivity of 72% at 800 °C, being comparable to those of our TiO2-doped SCS catalyst (Fig. 4C). However, at 700 °C it almost loses the activity (less than 6% CH₄ conversion) and achieves a poor C₂-C₃ selectivity of less than 30% (Fig. 4D). These distinct results solidly evidence that TiO₂-doping remarkably enhances the low-temperature OCM activity/ selectivity of the Mn₂O₃-Na₂WO₄/SiO₂. In addition, the OCM product distributions (21.3% C_2H_6 , 43.5% C_2H_4 , 3.3% C_3H_8 , and 2% C_3H_6) for the 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800 catalyst at 700 $^\circ\text{C}$ using a feed gas of CH₄:O₂:N₂ = 5:1:4 and a GHSV of 8000 mL $g_{cat.}^{-1}\,h^{-1}$ are shown in Fig. S1, and the effects of reaction conditions and catalyst preparation parameters on the product distributions are also investigated with the results as shown in Table S1 and Table S2. Clearly, the product distribution is sensitive to the reaction conditions (especially the reaction temperature and GHSV) but not to the catalyst preparation parameters studied. With the increase in either the reaction temperature or GHSV, ethylene formation is favourable thereby leading to an increase in the ratio of ethylene to ethane. Tuning the CH_4/O_2 ratio makes the product distributions changed a little, whereas the ratio of ethylene to ethane remains almost constant at ~ 2 at 700 °C in the

whole CH₄/O₂ ratio investigated.

3.3. Insight into the TiO_2 -doping chemistry in low-temperature OCM catalysis: XRD and Raman studies

To allow the above evidenced low-temperature activity improvement effect by TiO_2 -doping to be optimized and exploited more rationally in the future work, it is imperative to explore the TiO_2 -doping catalysis of the OCM reaction. To accomplish this goal, XRD and Raman techniques were employed to track the bulk and surface evolution behaviors of the 6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalysts before and after TiO₂-doping. The used catalysts were particularly characterized and analyzed because of the inevitable reconstruction of the surface even bulk phase.

The freshly-synthesized, calcined, and used samples of the $6-Mn_2O_3$ -10- Na_2WO_4/SiO_2 and $6-TiO_2$ -I- $6-Mn_2O_3$ -10- Na_2WO_4/SiO_2 catalysts were characterized by XRD, and their patterns are shown in Fig. 5. For the freshly-synthesized samples (patterns a and b), no any characteristic diffraction peak of Ti-, Mn-, Na-, and/or W- containing compounds is observable but a dispersing peak for amorphous SiO₂ at 2 theta of 23.3°, indicating the high dispersion of these species. After calcination at 800 °C in air for 4 h (patterns c and d), amorphous SiO₂ is transformed



Fig. 5. XRD patterns of fresh as-synthesized samples without (a) and with (b) TiO₂-doping, catalysts after calcining at 800 °C without (c) and with (d) TiO₂-doping, used catalysts without (e) and with (f) TiO₂-doping. Reaction conditions: 1.0 g catalyst, 700 °C, GHSV of 8000 mL g_{cat}⁻¹ h⁻¹, CH₄/O₂/N₂ molar ratio of 5/1/4, atmospheric pressure. Note of SCS preparation: see that in Fig. 1. Note of catalyst activation: see that in Fig. 2.

into a-cristobalite, tridymite and/or some quartz whereas phases of Na₂WO₄, Mn₂O₃ and MnWO₄ appear; interestingly, XRD peaks of MnWO₄ phase are stronger for the 6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalyst than for the 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalyst (patterns c and d), suggesting that the MnWO₄ formation is more preferable in the former than in the latter during the calcination treatment at 800 °C. After reaction (at 800 °C for 2 h and subsequently at 700 °C for another 0.5 h), no appearance of new compound phase is observable on the used 6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalyst whereas the MnWO₄ phase peaks become stronger compared to the calcined one (patterns c and e); in contrast, on the used 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalyst, a new phase formation of MnTiO₃ compound is evidently detectable by XRD while the peak intensity of MnWO₄ is in turn weakened in comparison with the used 6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalyst (patterns e and f). Regarding the Na₂WO₄, its role in improving the selectivity and promoting the transformation from amorphous SiO₂ to a-cristobalite in the OCM reaction has been widely confirmed and accepted in a large number of studies [25,26]. In combining this information with the fact that the TiO2-doped catalyst achieved satisfying low-temperature OCM activity (e.g., at or even below 700 °C), it is rational to infer that the formation of MnTiO₃ is paramount for the dramatic improvement of the catalyst low-temperature activity.

To further verify the promotion effect of $MnTiO_3$ on the low-temperature activity, the catalysts with increased TiO_2 plus Mn_2O_3 loading (Ti/Mn ratio of 1:1 to correspond to $MnTiO_3$ formation) from 4 to 20 wt %, after undergoing the OCM reaction as in the Section of 3.2.2, were also characterized by the XRD. The XRD patterns are shown in Fig. 6A as well as the part of 2 theta from 30 to 40° magnified in Fig. 6B. Clearly, formation of $MnTiO_3$ compound is observed on all these used catalysts and its peak intensity is monotonously increased with the increase in the TiO_2 plus Mn_2O_3 loading from 4 to 20 wt%. As show in Fig. 3A, at 700 °C the CH₄ conversion and C_2 - C_3 selectivity are respectively promoted from 15 to 20% and 55–70% along with the increase in the TiO_2 plus Mn_2O_3 loading from 4 to 12 wt%, and then illustrate a plateau with further increasing it up to 20 wt%. No doubt that the MnTiO₃ formation is essential to improve the catalyst low-temperature activity but in a certain amount range.

It is noted that, prior to reacting at 700 °C for 0.5 h, these catalysts all undergo OCM reaction at 800 °C for 2 h and therefore the MnTiO₃ compounds are already formed. If directly reacting at 700 °C, the 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalyst, quite similar to the non-TiO₂-doped one (Fig. 4D), delivers a very low CH₄ conversion (6%) with a C₂-C₃ selectivity of only 28% because no any MnTiO₃ compound is formed (Fig. 6B). After elevating this TiO₂-doped catalyst bed temperature to 800 °C and running the OCM reaction for 2 h, not surprisingly, the formation of MnTiO₃ compound is clearly observed (Fig. 6B). Accompanied with the formation of MnTiO₃ compound, interestingly, this TiO₂-doped catalyst become highly active and selective at low temperature of 700 °C, achieving a high CH₄ conversion of 20% with a high C₂-C₃ selectivity of 70% (Fig. 6B).

The Raman spectroscopy was also employed to monitor the catalyst surface. The Raman spectra for the pure $MnTiO_3$, Mn_2O_3 and $MnWO_4$ compounds were recorded as reference, which are displayed in Fig. 7A. On the used 6-TiO_2-I-6-Mn_2O_3-10-Na_2WO_4/SiO_2 catalyst after reaction

at 800 °C for 2 h and then at 700 °C for another 0.5 h, a MnTiO3-enriched surface is observed with some Na₂WO₄, TiO₂ and α -cristobalite but no any Mn₂O₃ is detected (Fig. 7B, spectrum a). On the used 6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalyst, the surface is dominated by MnWO₄ with detectable α -cristobalite and Na₂WO₄ (Fig. 7B, spectrum b). When directly running at 700 °C, both catalysts with and without TiO₂-doping show comparable but poor activity and selectivity, and meanwhile, similar Raman spectra are observed on their surfaces, which are very close to the pure Mn₂O₃ sample (Fig. 7C). After undergoing the OCM reaction at 800 °C for 2 h and then at 700 °C for 0.5 h, a MnTiO3-enriched surface appears on the 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalvst (Fig. 7C), associated with a sharp increase of CH₄ conversion from 6% to 20% and C_2 - C_3 selectivity 28% to 70% (Fig. 6B). The above Raman-indicated MnTiO₃-enriched surface formation in correspondence to the high CH₄ conversion and high C₂-C₃ selectivity solidly confirms again that MnTiO₃ governs the low-temperature OCM activity for our TiO₂-doped Mn₂O₃-10-Na₂WO₄/SiO₂ catalysts.

3.4. Stability

Stability is a very critical practical consideration for a heterogeneous catalyst. At 700 °C and a total GHSV of 8000 mL $g_{cat.}^{-1} h^{-1}$, as shown in Fig. 8A, the 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂ catalyst is stable for at least 250 h without deactivation sign for a feed gas of CH₄:O₂:N₂ = 5:1:4; the CH₄ conversion remains at 19–21% throughout entire 250 h testing while C₂-C₃ selectivity is retained at 68–72% with an ethylene/ethane ratio of 2. After 250 h testing, the used catalyst was also characterized by XRD and Raman, with the results as shown in Fig. 8B,C. Clearly, the bulk phase and surface compositions almost maintain unchanged even after 250 testing, compared to those at the beginning (Fig. 5, XRD pattern a; Fig. 7B, Raman spectrum a). Most notably, the bulk phase of formed MnTiO₃ is sustained with a MnTiO₃enriched surface throughout the 250 h testing (Fig. 8B,C), which is critical to assure the promising activity/selectivity maintenance.

4. Conclusions

Low-temperature active, selective and stable Ti-doped Mn_2O_3 - Na_2WO_4/SiO_2 catalyst has been developed through the SCS method for the OCM reaction. The most promising catalyst, with 6 wt% TiO₂, 6 wt % Mn_2O_3 and 10 wt% Na_2WO_4 , is obtained using titanium isopropoxide (Ti-I) as Ti precursor, ϕ of 2 and calcination temperature of 800 °C. This catalyst, activated by undergoing the OCM at 800 °C for 2 h, achieves a high CH₄ conversion of ~20% with a high C₂-C₃ selectivity of ~70% and is stable for at least 250 h at 700 °C and GHSV of 8000 mL g_{cat.}⁻¹ h⁻¹ for a feed gas of CH₄:O₂:N₂ = 5:1:4. Both XRD and Raman results consistently reveal that bulk MnTiO₃ phase is formed during the OCM process in association with a derived MnTiO₃-enriched catalyst surface, which appears to be important for the dramatic improvement of catalyst low-temperature activity for the OCM reaction.

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Fig. 6. (A) XRD patterns of the TiO₂-I-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800 catalyst with various loadings of TiO₂ plus Mn₂O₃ after undergoing the OCM reaction at 800 °C for 2 h and then at 700 °C for 0.5 h. (B) XRD patterns, CH₄ conversion (C_{CH4}) and C_2 - G_3 selectivity (S_{C2-C3}) for the 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/SiO₂-2-800 catalysts after undergoing the OCM reaction first directly at 700 °C for 0.5 h (top) and subsequently at 800 °C for 2 h then at 700 °C for another 0.5 h (bottom). Reaction conditions: 1.0 g catalyst, GHSV of 8000 mL g_{cat.}⁻¹h⁻¹, CH₄/O₂/N₂ molar ratio of 5/1/4, atmospheric pressure.



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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2017.07.012.

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Fig. 7. Raman spectra of the various samples. (A) Pure Mn_2O_3 , $MnWO_4$, and $MnTiO_3$, (B) used 6-TiO_2-1-6- Mn_2O_3 -10- Na_2WO_4 /SiO_2-2-800 (a) and 6- Mn_2O_3 -10- Na_2WO_4 /SiO_2-2-800 (b) catalysts after undergoing the OCM reaction at 800 °C for 2 h then at 700 °C for another 0.5 h. (C) 6-TiO_2-1-6- Mn_2O_3 -10- Na_2WO_4 /SiO_2-2-800 catalyst after undergoing the OCM reaction first directly at 700 °C for 0.5 h (top) and subsequently at 800 °C for 2 h then at 700 °C for another 0.5 h (bottom). Reaction conditions: 1.0 g catalyst, GHSV of 8000 mL g_{cat.} $^{-1}h^{-1}$, CH₄/O₂/N₂ molar ratio of 5/1/4, atmospheric pressure.

Fig. 8. (A) CH₄ conversion and C₂-C₃ selectivity for the OCM reaction against the time on stream at 700 °C using the 6-TiO₂-I-6-Mn₂O₃-10-Na₂WO₄/ SiO₂-2-800 catalyst. (B) XRD pattern and (C) Raman spectrum of the catalyst after 250 h OCM reaction testing. Note of catalyst activation: see that in Fig. 2. Reaction conditions: catalyst of 1.0 g, GHSV of 8000 mL g_{cat.}⁻¹ h⁻¹, CH₄/O₂/N₂ molar ratio of 5/1/4, atmospheric pressure.

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