



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic performance of Na-Mn₂O₃-based catalysts towards oxidative coupling of methane

P. Saychu^a, M. Thanasiriruk^a, C. Khajonvittayakul^a, R. Viratikul^a, V. Tongnan^a, M. Hartley^b, S. Wongsakulphasatch^b, N. Laosiripojana^c, U.W. Hartley^{a,*}

^a Department of Chemical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok, Bangkok (KMUTNB), 1518 Pracharaj 1 Rd., Wongsawang, Bangsue, Bangkok, 10800, Thailand

^b Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, 10800, Thailand

^c The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi (KMUTT), 126 Pracha Uthit Rd., Bang Mod, Thung Khru, Bangkok, 10140, Thailand

ARTICLE INFO

Keywords:

Oxidative coupling of methane
Ethylene
Catalysts
Metal oxide
Alkali chloride

ABSTRACT

Various active materials (NaCl and Na₂WO₄ doped on Mn₂O₃) and supports (SiC, SiO₂, WO₄, CoO, La₂O₃, Ce₂O₃, ZnO, Al₂O₃, Cr₂O₃, La_{0.3}Sr_{0.7}Cr_{0.7}Fe_{0.3}O_{3.8} (LSCF), and clinker) were prepared and tested for use in the OCM reaction in a packed-bed reactor. NaCl-Mn₂O₃/SiO₂ showed the best performance among the catalysts, with 37.5 % methane conversion, 60.5 % C₂ selectivity, and 22.7 C₂ yield at an optimum temperature of 750 °C under atmospheric pressure. The ethylene-to-ethane ratio of NaCl-Mn₂O₃/SiO₂ (7.5) was found to be the highest, and higher than that of Na₂WO₄-Mn₂O₃/SiO₂ (1.4), possibly due to its high basicity. Na₂WO₄-Mn₂O₃/SiO₂ showed good catalytic stability during 12 h time-on-stream experiment whereas slight deactivation was observed in NaCl-Mn₂O₃/SiO₂ due to the decomposition of NaCl, evidenced from traces of gaseous chloride compounds such as CH₃CH₂Cl, CH₃Cl, and Cl₂ in the outlet stream. However, the degree of deactivation was found to be more severe when (1) level of NaCl was lower (from 60 % to 10 %) and (2) time-on-stream experiment was tested for the longer period of time (12 h–62 h). The loss of chloride was estimated at 57 and 69 % (by weight) after 12 and 62 h TOS, respectively. The results were in good agreement with information received from XRD where Na₂SiO₃ was observed due to the loss of chloride, when the deactivation was extreme. From O₂-TPSR result, Na₂WO₄-Mn₂O₃/SiO₂ showed no coke deposition, which could be the result of the high surface oxygen (O_s) contained in Na₂WO₄. Carbon formation at 56.36 μmol/g.hr was detected when using NaCl-Mn₂O₃/SiO₂ as catalyst. The solid-gas mechanism of the catalytic OCM reaction was predicted using the CH₄-TPSR technique.

1. Introduction

Methane is a well-known intermediate/raw material for the production of highly valuable chemicals (ethane, ethylene, and methanol) and fuels (synthesis gas, synthetic liquid fuels) and has applications in energy and energy storage technologies (power generation, H₂ storage) [1–5]. Apart from conventional fossil fuels, methane is widely available from other alternative sources, such as shale gas or biogas [2,3]. One of the highest valued products that could be produced from methane is ethylene, which can be produced via either direct processes (i.e., oxidative coupling of methane (OCM)) or indirect processes (i.e., Fischer-Tropsch or methanol to olefins (MTO)) [4,7–10]. The OCM has several advantages over other processes, i.e., (1) lower operating

temperature than that used for steam reforming, (2) lower operating pressure than those of Fischer-Tropsch or MTO, and (3) single-step operation. In general, the OCM involves 2 minor reactions, as shown in Eqs. (1) and (2) [6]:



The performance of the OCM process is found to depend on various parameters, i.e., operating conditions, catalyst, and/or residence time [8]. A common issue in catalysis is low yield, which is the main challenge for successful OCM processes [4,11–13]. Solids such as CaO/CeO₂

* Corresponding author.

E-mail addresses: Unalome.w.cpe@tggs-bangkok.org, unalomew@kmutnb.ac.th (U.W. Hartley).

<https://doi.org/10.1016/j.cattod.2020.12.024>

Received 1 December 2019; Received in revised form 23 November 2020; Accepted 1 December 2020

Available online 19 January 2021

0920-5861/© 2021 Elsevier B.V. All rights reserved.

[14], Li/MgO [15], Li-Mn/WO₃/TiO₂ [16], perovskites [17], and Na₂WO₄/Mn/SiO₂ [2,12,18–22] have been shown to be active in the OCM reaction. They showed good OCM performance in a fixed-bed reactor or packed-bed reactor. Among these materials, Na₂WO₄/Mn/SiO₂ showed high selectivity and high stability towards OCM [2,12,18–22]. Na-containing compounds were believed to prevent total oxidation, while WO₄ contributed to good C₂₊ selectivity, which was suggested to enhance methane conversion due to its geometric properties [2,23,24]. However, Na₂WO₄ is thermally unstable when operated at temperatures higher than 650 °C [2]. Alkali chloride, such as NaCl, was found to promote C₂₊ selectivity while offering much better thermal stability, as it was proven to maintain its activity at 800 °C [23,25–27]. Mn presented high performance in terms of C₂₊ selectivity and methane conversion when compared with transition metals, i.e., V, Cr, or Zn, which showed poor performance [12]. Mn is good for OCM performance due to its electronic properties that can enhance electron transfer [12]. Metal oxides, i.e., TiO₂ and ZnO, contributed to the good C₂₊ selectivity [2,18,28]. SiO₂, SiC and several rare earth oxides have been reported as promising supports for the OCM process due to their good stability and high thermal conductivity [18,29,30]. As shown above, different solids play different roles in determining the OCM process performance. This work aimed to develop solid materials composed of different types of solids to enhance the performance of OCM reaction on NaCl-Mn₂O₃ or Na₂WO₄-Mn₂O₃ catalysts, where the solid materials are SiC, SiO₂, WO₄, CoO, La₂O₃, Ce₂O₃, ZnO, Al₂O₃, Cr₂O₃, LSCF, and clinker. In addition, the physical properties and stability were investigated. Finally, the mechanism of the optimum catalyst was discussed based on the results of CH₄-TPSR and O₂-TPSR.

2. Experiment

2.1. Catalyst preparation

The percentage of each Na compound (Na₂WO₄ and NaCl) was 60 % by mole, while Mn₂O₃ was fixed at 10 % of the overall catalyst systems. The ratio of Mn₂O₃ to other supports (i.e., SiC, SiO₂, WO₄, CoO, La₂O₃, Ce₂O₃, ZnO, Al₂O₃, Cr₂O₃, LSCF, and clinker) was fixed at 10 to 30 (% by mole). In addition, 10 % NaCl-Mn₂O₃/SiO₂ was also prepared, mainly for the Time-On-Stream experiment. For the nonsupport catalysts, such as NaCl-Mn₂O₃ and Na₂WO₄-Mn₂O₃, the molar ratio of Na-compound and Mn₂O₃ was kept at 9 to 1. La_{0.3}Sr_{0.7}Cr_{0.7}Fe_{0.3}O_{3.8} (LSCF) was prepared using the sol-gel method, and details of the preparation can be found in our previous work [31]. Commercial grade SiO₂ (98 %, Ajax Finechem), WO₄ (99 %, Aldrich), SiC (97.5 %, Aldrich), Al₂O₃ (KEMAUS), and clinker (SCG Company) were used in this work. The other metal oxides, i.e., La₂O₃, ZnO, CoO, Ce₂O₃, and Cr₂O₃, were prepared using the sol-gel method [32]. Relevant metal precursors, i.e., La(NO₃)₃·6H₂O (99 %, Himedia), Zn(NO₃)₂·6H₂O (99.9%, Ajax Finechem), Co(NO₃)₂·6H₂O (98 %, Carlon Erba), Ce(NO₃)₃·6H₂O (99 %, Aldrich), and Cr(NO₃)₃·9H₂O (99 %, ACROS) were added to 250 mL distilled water. A 5 mL aliquot of NH₃ (30%, Panreac) was added to the mixture and stirred continuously for 1 h. The resulting gel was centrifuged for 15 min at 3500 rpm. The supernatant was then discarded and rinsed with water before adding 125 mL of distilled water. The mixture was heated to 105 °C for 24 h to evaporate excess water before 20 mL of ethanol was added. The solid was separated again using centrifugation and then dried overnight at 65 °C. The resulting metal oxide was calcined at 400 °C for 11 h, where the temperature was increased from room temperature at a heating rate of 2 °C/min. The sample was then heated to 550 °C using a heating rate of 5 °C/min for another 9 h. NaCl-Mn₂O₃ and Na₂WO₄-Mn₂O₃ were prepared using the mixed slurry method [3]. Corresponding amounts of Na- (from either NaCl or Na₂WO₄) and Mn- (from Mn(NO₃)₂·4H₂O) were mixed into the above metal oxides, followed by the addition of 25 mL NH₃ solution under continuous stirring. The solution was then heated to 95 °C for 3 h and dried overnight at 110 °C. The resulting product was calcined at 400 °C

for 9 h. The catalysts were pelletized, crushed and sieved to a size of 75–180 micrometers.

2.2. OCM performance test

The catalytic performance of all the catalysts towards OCM was tested in a quartz tube packed bed reactor (I.D. = 10 mm, O.D. = 13 mm, length = 50 cm). A type K thermocouple was inserted along the wall of the reactor near the catalyst bed. Two grams of catalyst was packed inside the reactor between thin layers of quartz wool. The catalyst was calcined in situ at 750 °C for 2 h before undergoing the OCM reaction, where a mixed gaseous reactant of CH₄ (40 % CH₄/Ar, BIG) and O₂ (40 %, O₂/Ar, BIG) was introduced into the reactor at a ratio of 4 to 1 using mass flow controllers (Brooks instrument flow, 0–220 mL/min). Ar (99.995 %, BIG) was used as a make-up gas to keep the total flow rate at 50 mL/min. The operating temperature was varied at 700, 750, 800, and 850 °C under atmospheric pressure. At the outlet stream, water was condensed using silica gel before being measured by a bubble flow meter. The dry gaseous products were analyzed using on-line gas chromatography (Shimadzu GC-2014, FID-TCD detector) coupled with a Porapak Q capillary column. The catalytic performance of each catalyst, such as methane conversion, C₂ selectivity, C₂ yield and ratio of ethylene and ethane, was evaluated using the following equations:

$$\text{CH}_4\text{conversion}(\%) = \frac{\text{mole of CH}_4\text{ consumed}}{\text{mole of CH}_4\text{ in the feed}} \times 100 \quad (3)$$

$$\text{C}^{2+}\text{selectivity}(\%) = \frac{\text{moles of C}^{2+}\text{ hydrocarbon in product stream}}{\text{moles of CO}_2, \text{CO}, \text{C}_2\text{H}_6, \text{C}_2\text{H}_4\text{ in product stream}} \times 100 \quad (4)$$

$$\text{C}^{2+}\text{yield}(\%) = \frac{\text{CH}_4\text{conversion}(\%) \times \text{C}^{2+}\text{selectivity}(\%)}{100} \quad (5)$$

$$\text{Ratio of ethylene to ethane} = \frac{\text{mole of C}_2\text{H}_4}{\text{mole of C}_2\text{H}_6} \quad (6)$$

The carbon balance was also calculated to validate the experimental accuracy.

$$\text{Carbon difference} = \text{carbon inlet} - \text{carbon outlet} \quad (7)$$

Where carbon inlet = mole of CH₄ at inlet, and carbon outlet = mole of CH₄ + CO₂ + CO + (2C₂H₆) + (2C₂H₄) at outlet

The stability of the catalysts was tested for 12 h via the time on stream (TOS) under the optimal conditions obtained from the catalytic performance experiment.

2.3. Material characterization

2.3.1. X-ray diffraction

The crystallinity of the samples both pre- and post-exposure was analyzed and compared using X-ray diffraction (XRD) analysis (Bruker D8 Advance) with CuKα (λ = 1.5418 Å) radiation at a scanning speed of 0.01°/s for 2θ ranging from 5° to 80°. A semi-quantitative analysis was carried out in situ using EVA software. The percentage of each phase in the samples was obtained.

2.3.2. O₂-temperature programmed surface reaction

Carbon deposition on the catalyst's surface was also studied after the catalyst was spent in the time on stream experiment using the O₂-temperature programmed surface reaction (O₂-TPSR) technique, where 40 % O₂/Ar was fed into the packed-bed reactor while the reactor's temperature was increased by 5 °C/min from room temperature to 850 °C at 50 mL/min of the total flow rate.

2.3.3. Temperature programmed desorption of oxygen

The temperature-programmed desorption of oxygen (O₂-TPD) was applied to determine the oxygen capacity/mobility of the catalysts. Two grams of each catalyst was pretreated in oxidizing gas, 10 % O₂/Ar (100 ml/min), at 700 °C for 1 h and then cooled to ambient temperature. The excess/physorption of oxygen on the catalyst surface was eliminated by Ar flushing. O₂ desorption was carried out in the presence of 100 ml/min of pure Ar (99.995 %, BIG), while the temperature was ramped up from room temperature to 850 °C at a heating rate of 5 °C/min. The oxygen release was analyzed in real time using an on-line quadrupole mass spectrometer (MS, (Omnistar, GSD 320 O1 Model)).

2.3.4. CH₄-temperature programmed surface reaction

Gas-solid interactions between the reactants and catalyst surface were investigated using the CH₄-temperature programmed surface reaction (CH₄-TPSR) technique. CH₄/Ar (5%) was fed into the reactor while the temperature was increased by 5 °C/min from room temperature to 850 °C. The gaseous product stream was analyzed using a quadrupole mass spectrometer based on the following mass-to-charge ratio: H₂ (2), CH₄ (16), C₂H₄ + C₂H₆ (27), CO + C₂H₄ + C₂H₆ (28), C₂H₆ (30), CO₂ (44), CH₃Cl (50), CH₃CH₂Cl (64) and Cl₂ (70).

3. Results and discussion

3.1. Catalytic performance test

All the prepared catalysts were tested at different operating temperatures, varying from 700 to 850 °C, giving the CH₄ conversion, C₂ selectivity, C₂ yield, and C₂H₄/C₂H₆ ratios shown in Table 1. Without supports, NaCl-Mn₂O₃ was found to show better performance than Na₂WO₄-Mn₂O₃ at all experimental temperatures. SiO₂, when added as a support to either NaCl or Na₂WO₄, was found to increase the catalyst system performance. This result agreed with the results of other studies [18]. The selection of the support was also found to play an important role. When NaCl-Mn₂O₃ was chosen as the active site, SiO₂ showed the best performance as a support, while the perovskite LSCF showed the worst performance, as illustrated in Table 1 and Fig. 1. In terms of the effect of support on the optimal operating temperature, SiO₂ showed the lowest operating temperature of 750 °C, whereas Al₂O₃, Ce₂O₃, WO₄, clinker, and SiC had an optimal operating temperature of 800 °C. LSCF, ZnO, CoO, Cr₂O₃ and La₂O₃ can be optimally operated at 850 °C, the highest temperature in the range. These results are in good agreement with previous research reported by [33].

The process performance of each catalyst at its optimal operating temperature was plotted together for comparison purposes, as shown in Figs. 1 and 2. NaCl-Mn₂O₃ was found to have much better catalytic performance than Na₂WO₄-Mn₂O₃. NaCl-Mn₂O₃ exhibited 30.1 % methane conversion, 53.4 % C₂ selectivity, 16.1 % C₂ yield, and ethylene-to-ethane ratio of 3.2 at 800 °C, whereas methane conversion, C₂ selectivity, C₂ yield, and ratio of ethylene to ethane over Na₂WO₄-Mn₂O₃ were found to be 11.7 %, 29.9 %, 3.5 %, and 1.3, respectively, at 850 °C.

In terms of the catalyst supports, only SiO₂ was found to enhance the catalytic performance of NaCl-Mn₂O₃ in all aspects. NaCl-Mn₂O₃/SiO₂ offered a methane conversion, C₂ selectivity, C₂ yield, and ratio of ethylene to ethane of 37.5 %, 60.5 %, 22.7 %, and 7.5, respectively, at an optimum temperature of 750 °C. SiO₂ was reported to improve the mobility of surface-active oxygen (O_s) (Eq. (8)), which enhanced the overall catalytic performance [33,34].



Where V_s^{••} represents oxygen vacancy.

The methane conversion achieved from all catalysts was lower than 40 % due to the limitation of O₂ to improve the C₂ selectivity [35]. NaCl-Mn₂O₃ showed the best performance towards CH₄ activation [25,

Table 1

Catalytic performance of each catalyst at different operating temperatures.

Catalysts	Temperature (°C)	CH ₄ Conversion (%)	C ₂ selectivity (%)	C ₂ yield (%)
Na ₂ WO ₄ -Mn ₂ O ₃ /SiO ₂	700	2.5	30.1	0.8
	750*	19.5	45.6	8.9
	800	21.8	40.1	8.7
NaCl-Mn ₂ O ₃ /SiO ₂	850	20.5	33.3	6.8
	700	33.9	52.7	17.8
	750 ^a	37.5	60.5	22.7
NaCl-Mn ₂ O ₃ /Al ₂ O ₃	800	34.2	50.8	17.4
	850	27.9	36.0	10.0
	700	4.6	0.8	0.1
NaCl-Mn ₂ O ₃ /Ce ₂ O ₃	750	11.9	4.6	0.7
	800 ^a	17.1	22.8	4.6
	850	15.2	22.4	3.7
NaCl-Mn ₂ O ₃ /WO ₄	700	12.8	1.2	0.2
	750	12.5	3.3	0.4
	800 ^a	20.3	31.2	6.3
NaCl-Mn ₂ O ₃ /ZnO	850	17.1	27.9	4.8
	700	15.2	61.0	9.3
	750	18.9	51.0	9.6
NaCl-Mn ₂ O ₃ /CoO	800 ^a	23.6	42.6	10.1
	850	25.0	34.5	8.6
	700	18.6	1.3	0.2
NaCl-Mn ₂ O ₃ /LSCF	750	19.9	4.7	0.9
	800 ^a	24.9	22.1	5.5
	850	22.0	17.3	3.8
NaCl-Mn ₂ O ₃ /SiC	700	10.4	2.2	0.2
	750	20.1	28.9	5.8
	800 ^a	30.1	53.4	16.1
NaCl-Mn ₂ O ₃ /Cr ₂ O ₃	850	4.9	1.9	1.7
	700	14.8	25.4	3.8
	750	30.1	50.4	15.2
NaCl-Mn ₂ O ₃ /La ₂ O ₃	800 ^a	32.4	47.6	15.4
	850	26.8	25.8	6.8
	700	3.4	67.3	2.3
NaCl-Mn ₂ O ₃ /ZnO	750	3.9	19.6	0.8
	800	7.2	25.8	1.9
	850 ^a	11.7	29.9	3.5
NaCl-Mn ₂ O ₃ /LSCF	700	13.1	0.3	0.0
	750	11.1	0.6	0.1
	800	14.2	8.1	1.2
NaCl-Mn ₂ O ₃ /Cr ₂ O ₃	850 ^a	14.7	7.7	1.1
	700	14.4	2.0	0.3
	750	13.3	2.9	0.4
NaCl-Mn ₂ O ₃ /CoO	800	15.3	12.7	2.0
	850 ^a	20.5	23.6	4.8
	700	16.8	1.1	0.2
NaCl-Mn ₂ O ₃ /La ₂ O ₃	750	10.7	0.9	0.1
	800	11.7	8.6	1.0
	850 ^a	22.4	34.8	7.8
NaCl-Mn ₂ O ₃ /Cr ₂ O ₃	700	18.3	0.3	0.1
	750	19.6	2.0	0.4
	800	19.8	4.9	1.0
NaCl-Mn ₂ O ₃ /La ₂ O ₃	850 ^a	22.7	13.3	3.0
	700	17.8	16.0	2.8
	750	22.5	27.5	6.2
NaCl-Mn ₂ O ₃ /SiO ₂	800	22.2	23.4	5.2
	850 ^a	24.0	33.6	8.2

^a Optimal temperatures chosen in Fig. 1.

36].

However, many works from recent years reported Na₂WO₄-Mn₂O₃/SiO₂ as one of the best catalysts for OCM reaction, when Na₂WO₄ was doped at a much lower level (1% by mole) [22,37] compared to our work (60 % by mole). Table 2 below therefore compares catalytic performance of NaCl-Mn₂O₃/SiO₂ and Na₂WO₄-Mn₂O₃/SiO₂ at different percentage of dopants. 60 %NaCl-Mn₂O₃/SiO₂ showed the highest CH₄ conversion and ethylene-to-ethane ratio, estimated at 37.5 % and 7.5, respectively. The results agreed with previous work [25,38] which reported the positive influence of NaCl on conversion of ethane to ethylene as NaCl enhanced basicity of the catalyst system, leading to an alteration of active surface and its electronic configuration. On the other hand, C₂ selectivity and yield obtained over NaCl-Mn₂O₃/SiO₂ were not the best,

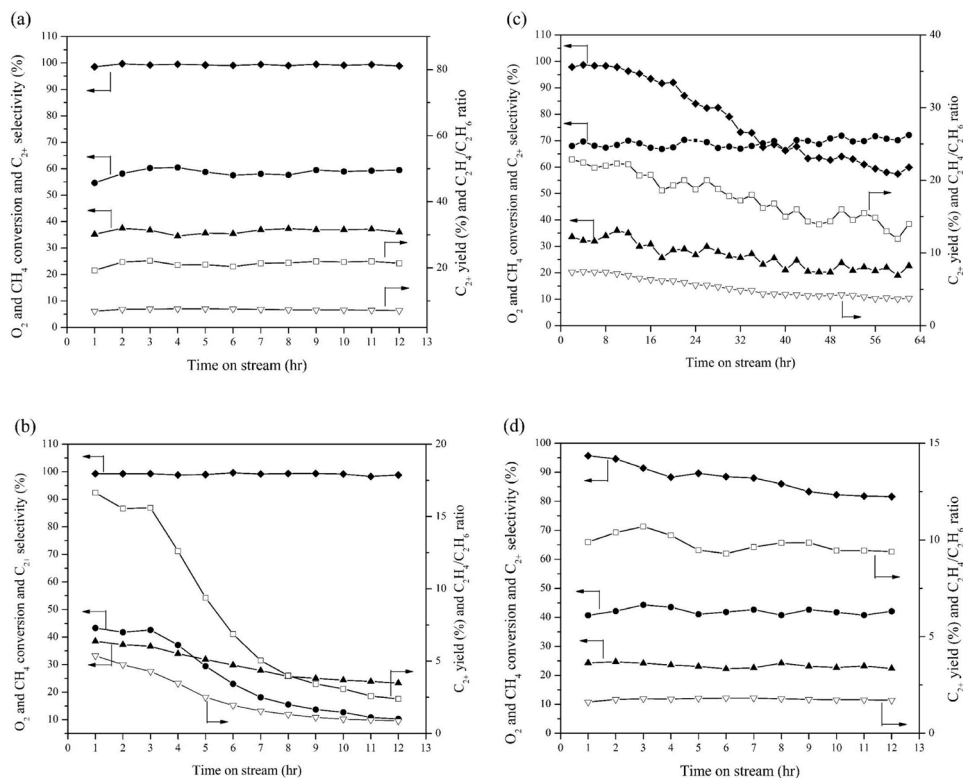
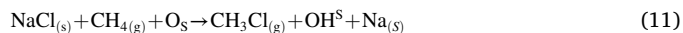
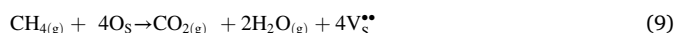


Fig. 3. Time-on-Stream of the OCM reaction over 2 g of; 60 %NaCl-Mn₂O₃/SiO₂ for 12 h (a), 10 %NaCl-Mn₂O₃/SiO₂ for 12 h (b), 60 %NaCl-Mn₂O₃/SiO₂ for 62 h (c), and 60 %Na₂WO₄-Mn₂O₃/SiO₂ for 12 h; at 750 °C. The total flow rate was 50 mL/min with a feed ratio of CH₄:O₂ fixed at 4; O₂ conversion (◆), CH₄ conversion (▲), C₂ selectivity (●), C₂ yield (□) and ratio of C₂H₄/C₂H₆ (▽) were measured.

generally indicating surface oxygen (O_s) [16,20], occurred at 400 °C and 500 °C for 60 %NaCl-Mn₂O₃/SiO₂ and 60 %Na₂WO₄-Mn₂O₃/SiO₂, respectively. The results agreed with the catalytic performance test, reported in Table 1, indicating that NaCl-Mn₂O₃/SiO₂ can be operated at lower temperature to achieve the same level of catalytic performance. The oxygen desorption amount of 60 %NaCl-Mn₂O₃/SiO₂ was estimated to be 278 μmol/g, whereas that of 60 %Na₂WO₄-Mn₂O₃/SiO₂ was 213 μmol/g.

3.4. CH₄-TPSR characterization

The OCM reaction mechanism over 60 %NaCl-Mn₂O₃/SiO₂ and 60 %Na₂WO₄-Mn₂O₃/SiO₂ was predicted using the CH₄-TPSR technique, where 40 % CH₄/Ar was fed into the packed bed reactor while the temperature was increased from room temperature to 850 °C. Figs. 6 and 7 represent the CH₄-TPSR results of 60 %NaCl-Mn₂O₃/SiO₂ and 60 %Na₂WO₄-Mn₂O₃/SiO₂, respectively. Both catalysts exhibit similar mechanistic pathways, which were divided into 4 regions depending on the operating temperature. In region I, there was no methane consumption where the temperature was lower than 300 °C. Methane conversion started to occur when the temperature ramped from 300 to 650 °C, region II, resulting in formation of CO₂, H₂O and C₂H₆. A surface methane combustion (where gaseous methane reacted with surface oxygen on Mn₂O₃ (Eq. 9)) and methane adsorption-dissociation reaction (where gaseous methane reacted with the active site on NaCl and/or Na₂WO₄) to form methyl radicals and hydrogen (Eq. (10)) [27] occurred in this temperature range. Methyl radicals started to form in the NaCl-Mn₂O₃/SiO₂ catalyst were produced by CH₃Cl cracking following Eqs. (11) and (12), where CH₃Cl occurred on the catalyst's surface (Fig. 6). Methane radicals were subsequently desorbed/released into the gas phase to form gaseous C₂H₆ (Eq. (13)) [9,38].



In region III in the temperature range of 650–850 °C, CH₄ was found to be greatly converted to gaseous compounds of $m/z = 2$ (H₂), $m/z = 27$ (C₂H₆ and C₂H₄), $m/z = 28$ (CO, C₂H₆ and C₂H₄), $m/z = 30$ (C₂H₆), $m/z = 44$ (CO₂), $m/z = 50$ (CH₃Cl), $m/z = 64$ (CH₃CH₂Cl) and $m/z = 70$ (Cl₂). The possible mechanistic pathways were assumed and proposed after all the m/z ratio was theoretically de-convoluted. During temperature from 650 to 750 °C, region III, C₂H₆, C₂H₄ and CO were all overlapped and found at m/z ratio = 27 and 28. However, C₂H₆ was separately presented at m/z ratio = 30 solely. In this region, C₂H₆ was produced first (Eq. (13)), before being dehydrogenated further to form C₂H₄ via heterogeneous catalytic oxidation of ethane (Eq. (14)) and thermal gas-phase dehydrogenation of ethane (Eq. (15)). Therefore, m/z ratio = 30 represented the un-converted C₂H₆. At temperature lower than 750 °C, the trend of both C₂H₆ and C₂H₄ production was increased when the temperature increased. These trends were confirmed and verified using GC (Shimadzu GC-2014ATP, coupled with TCD/FID detectors). In addition, C₂H₄ can also be produced in another way on the NaCl-Mn₂O₃/SiO₂ catalyst with CH₃CH₂Cl as an intermediate, where a chlorine radical catalyzed the CH₃CH₂Cl to synthesis ethylene from ethane (Eqs. (16) and (17)) [37].



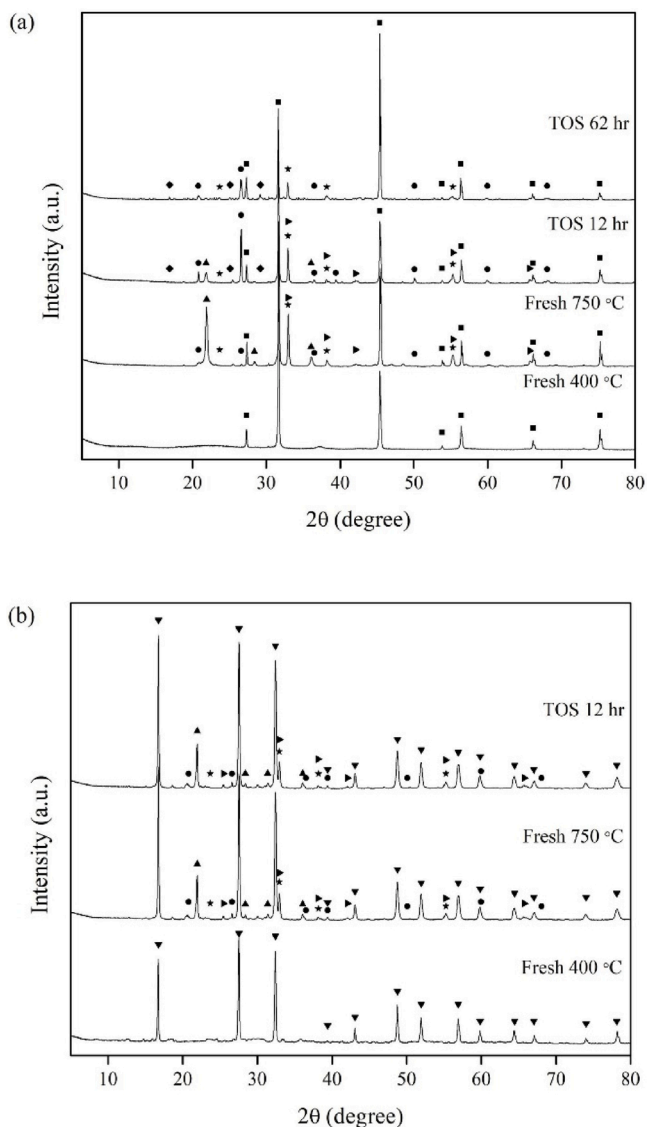
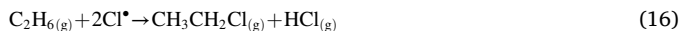


Fig. 4. XRD pattern results of 60 %NaCl-Mn₂O₃/SiO₂ (a) and 60 %Na₂WO₄-Mn₂O₃/SiO₂ (b) comparing calcined at 400 °C (fresh), calcined at 750 °C (fresh), after 12 h time-on-stream (TOS 12 h) at 750 °C and after 62 h time-on-stream (TOS 62 h) at 750 °C; NaCl (■), Na₂WO₄ (▼), α-SiO₂ (●), SiO₂ Cristobalite (▲), Mn₂O₃ (★), Mn₇O₈SiO₄ (►) and Na₂SiO₃ (◆) were shown.



CO formation peak was overlapped with C₂H₄ and C₂H₆ at *m/z* ratio = 28, thus, its formation trend was also verified using the GC. CO formation was found to increase when temperature increased. CO formation occurred through methane partial oxidation (Eq. (18)) [5, 20, and 39] and reverse water gas shift (Eq. (19)) [8,40], while CO₂ was decreased/consumed. NaCl was suggested to be regenerated by rapid reaction of HCl, Na⁺ and OH⁻ (Eq. (20)), as HCl could be theoretically formed (Eq. (17)), although not detected in the experiment. Cl₂ was also observed (Eq. (21)). During this region III, all the products started to decrease due to no oxygen in the surface of the catalyst after 750 °C.



Table 3

Crystalline size of the catalysts, comparing fresh (calcined at 400 and 750 °C) and after reaction at 750 °C (TOS 12 h and TOS 62 h).

Catalyst	Crystalline size (nm)				
	2θ	Calcined at 400 °C (fresh)	Calcined at 750 °C (fresh)	After reaction at 750 °C (TOS 12 h)	After reaction at 750 °C (TOS 62 h)
60 %NaCl-Mn ₂ O ₃ /SiO ₂					
α-cristobalite	21.90°	–	41	33	–
SiO ₂					
α-SiO ₂	26.60°	–	–	72	44
NaCl	31.65°	64	73	69	65
Na ₂ SiO ₃	21.84°	–	–	N/A	31
Mn ₂ O ₃	32.95°	–	50	56	58
60 %Na ₂ WO ₄ -Mn ₂ O ₃ /SiO ₂					
α-cristobalite	21.92°	–	54	53	–
SiO ₂					
α-SiO ₂	26.60°	–	–	N/A	N/A
Na ₂ WO ₄	27.49°	50	53	53	–
Mn ₂ O ₃	32.42°	–	50.63	49.87	–

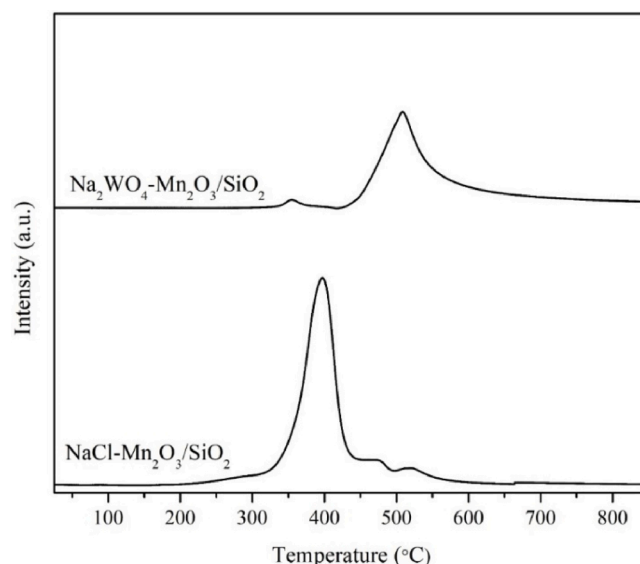
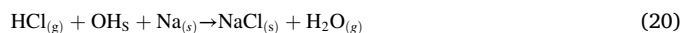


Fig. 5. The O₂-TPD of 60 %NaCl-Mn₂O₃/SiO₂ and 60 %Na₂WO₄-Mn₂O₃/SiO₂ catalyst.



In region IV where the temperature is higher than 850 °C, CH₄ cracking (Eq. (22)) was observed from the consumption of CH₄ and production of H₂, leading to the production of CO₂ via coke combustion (Eq. (23)). CO₂ production also occurred via C₂ combustion (Eq. (24)) [40,41]. Despite both catalysts sharing the similar mechanistic pathways, it was noticed that C₂H₆ and C₂H₄ occurred at the same temperature range for 60 %NaCl-Mn₂O₃/SiO₂, whereas, the C₂H₆ was observed first for 60 %Na₂WO₄-Mn₂O₃/SiO₂, then the C₂H₄ was produced afterwards [42].



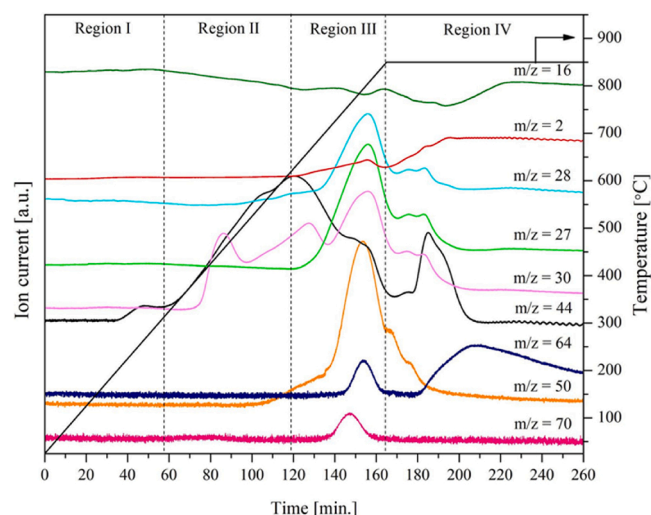


Fig. 6. The CH_4 -TPSR of $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ result exhibiting the gaseous product stream based on the following mass-to-charge ratio: H_2 ($m/z = 2$), CH_4 ($m/z = 16$), $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ ($m/z = 27$), $\text{CO} + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ ($m/z = 28$), C_2H_6 ($m/z = 30$), CO_2 ($m/z = 44$), CH_3Cl ($m/z = 50$), $\text{CH}_3\text{CH}_2\text{Cl}$ ($m/z = 64$) and Cl_2 ($m/z = 70$).

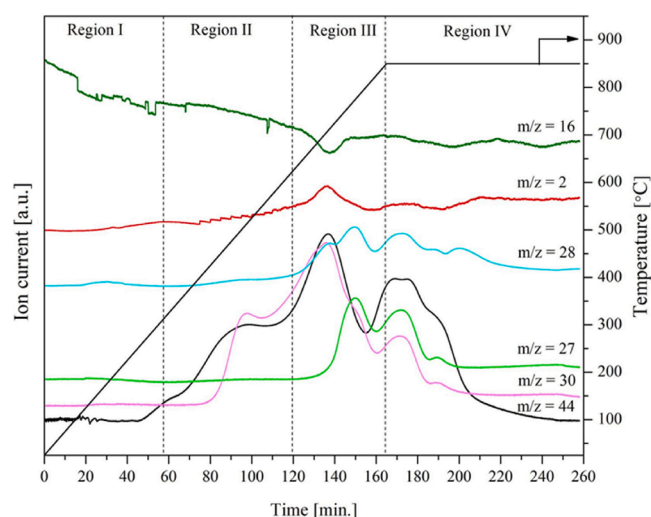


Fig. 7. The CH_4 -TPSR of $\text{Na}_2\text{WO}_4\text{-Mn}_2\text{O}_3/\text{SiO}_2$ result exhibiting the gaseous product stream based on the following mass-to-charge ratio: H_2 ($m/z = 2$), CH_4 ($m/z = 16$), $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ ($m/z = 27$), $\text{CO} + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ ($m/z = 28$), C_2H_6 ($m/z = 30$) and CO_2 ($m/z = 44$).

3.5. O_2 -TPSR characterization

Coke deposition of the post-exposure catalysts were investigated using O_2 -TPSR technique. Figs. 8 and 9 illustrate CO_2 and CO formation, occurred via coke combustion in the presence of the spent catalysts, respectively. Carbon balance was also calculated using the information received from the O_2 -TPSR, CH_4 -TPSR and TOS experiments. The amount of carbon in input and output stream was calculated using Eq. (7). Coke deposition were estimated from simple carbon balance amongst CO_2 , CO , CH_3Cl and $\text{CH}_3\text{CH}_2\text{Cl}$ as shown in Table 4. From Figs. 8 and 9, CO_2 and CO were found as the products of coke combustion over 60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$, regardless the time spent during the TOS (both 12 and 62 h), although amount of CO_2 and CO were increased when the TOS duration was increased from 12 to 62 h (from 0.5 to 1.8 $\mu\text{mol/g.hr}$). On the other hand, only CO_2 was detectable at 0.1 $\mu\text{mol/g.hr}$ over 10 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ (spent 12 h during TOS). No

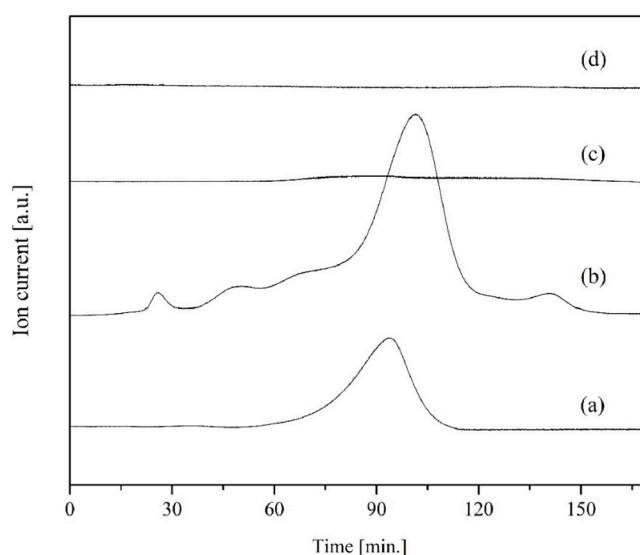


Fig. 8. CO_2 formation via coke combustion of the spent catalysts; 60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ after 12 h (a), 60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ after 62 h (b), 10 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ after 12 h (c), 60 % $\text{Na}_2\text{WO}_4\text{-Mn}_2\text{O}_3/\text{SiO}_2$ after 12 h (d).

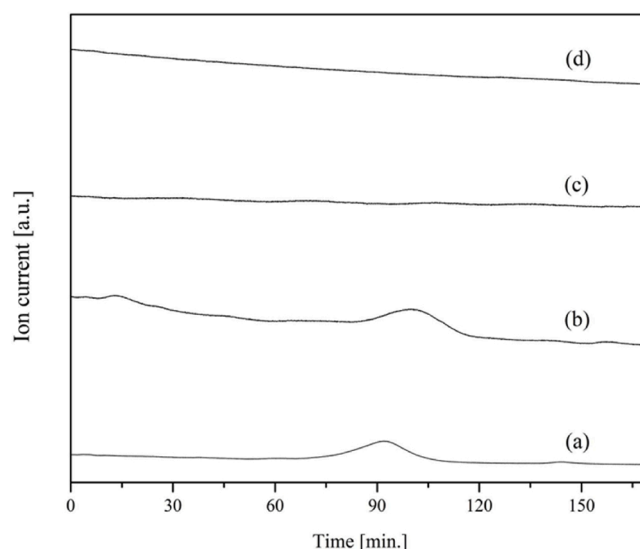


Fig. 9. CO formation via coke combustion of the spent catalysts; 60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ after 12 h (a), 60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ after 62 h (b), 10 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ after 12 h (c), 60 % $\text{Na}_2\text{WO}_4\text{-Mn}_2\text{O}_3/\text{SiO}_2$ after 12 h (d).

coke formation was observed for $\text{Na}_2\text{WO}_4\text{-Mn}_2\text{O}_3/\text{SiO}_2$. The results agree with the previous stability test of the catalysts.

4. Conclusion

60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ shows the highest CH_4 conversion, C_2 yield, C_2 selectivity and ethylene-to-ethane ratio amongst all the tested catalysts. Its stability is only comparable with $\text{Na}_2\text{WO}_4\text{-Mn}_2\text{O}_3/\text{SiO}_2$ (one of the most promising catalysts for OCM, reported by many researchers in the recent years) when the molar ratio of NaCl is as high as 60 %. Severe deactivation of $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ was observed when the concentration of NaCl is low, i.e. 10 % and/or (2) the TOS duration is longer, i.e. 62 h. The results are in good agreement with other experimental tests in this work. In the presence of 60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$, $\text{CH}_3\text{CH}_2\text{Cl}$, CH_3Cl and Cl_2 were detected during the CH_4 -TPSR transient experiment. Na_2SiO_3 was observed when the catalyst was exposed for 62 h of TOS

Table 4Carbon balance for OCM reaction over $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ and $\text{Na}_2\text{WO}_4\text{-Mn}_2\text{O}_3/\text{SiO}_2$, reported in $\mu\text{mol/g.hr}$.

Catalyst	Carbon Inlet (TOS)	Carbon Outlet (TOS)	Carbon Difference (TOS)	Coke Formation ($\text{O}_2\text{-TPSR}$)		Balanced CH_3Cl and $\text{CH}_3\text{CH}_2\text{Cl}(\text{CH}_4\text{-TPSR})$
60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ (12 h)	100	94.5	5.5	0.4	0.1	5.0
60 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ (62 h)	100	90.3	9.7	1.6	0.2	7.9
10 % $\text{NaCl-Mn}_2\text{O}_3/\text{SiO}_2$ (12 h)	100	98.2	1.8	0.1	N/A	1.7
60 % $\text{Na}_2\text{WO}_4\text{-Mn}_2\text{O}_3/\text{SiO}_2$ (12 h)	100	99.8	0.2	N/A	N/A	N/A

experiment. In future work, vaporized alkali chloride could considerably be added to the catalyst system to compensate the loss of chloride, or even be done through the recycle of the chloride vapor.

CRediT authorship contribution statement

P. Saychu: Writing - original draft, Investigation. **M. Thanasiruk:** Investigation, Methodology. **C. Khajonvittayakul:** Visualization, Data curation. **R. Viratikul:** . **V. Tongnan:** Visualization, Data curation, Methodology. **M. Hartley:** Formal analysis. **S. Wongsakulphasatch:** Investigation, Methodology. **N. Laosiripojana:** Resources, Validation. **U.W. Hartley:** Supervision, Writing - review & editing, Conceptualization, Funding acquisition.

Declaration of Competing Interest

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

Acknowledgment

This work was supported by Thailand Research Fund (RSA6180061), National Research Council of Thailand (NRCT-KMUTNB-GOV-63), Ministry of Higher Education, Science, Research and Innovation (NRCT-MHESI-130/2563), King Mongkut's University of Technology North Bangkok (KMUTNB-GEN-57-49, KMUTNB-GEN-59-65, KMUTNB-NEW-59-02, KMUTNB-BasicR-64-31) and PTT Public Company Limited.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.cattod.2020.12.024>.

References

- H. Wang, R. Schmack, B. Paul, M. Albrecht, S. Sokolov, S. Rummeler, E. V. Kondratenko, R. Kraehnert, Porous silicon carbide as a support for Mn/Na/W/SiC catalyst in the oxidative coupling of methane, *Appl. Catal. A Gen.* 537 (2017) 33–39.
- S. Gu, H. Oh, J. Choi, D.J. Suh, J. Jae, J. Choi, J. Ha, Effect of metal or metal oxide additives on oxidative coupling of methane using $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts: reducibility of metal additives to manipulate the catalytic activity, *Appl. Catal. A Gen.* 562 (2018) 114–119.
- A. Aseem, M.P. Harold, C_2 yield enhancement during oxidative coupling of methane in a nonpermeable porous membrane reactor, *Chem. Eng. Sci.* 175 (2018) 199–207.
- Y. Gambo, A.A. Jalil, S. Triwahyono, A.A. Abdulrasheed, Recent advance and future prospect in catalysts for oxidative coupling of methane to ethylene: a review, *J. Ind. Eng. Chem.* 59 (2018) 218–229.
- J.S. Ahari, S. Zarrinpashne, M.T. Sadeghi, Micro-kinetic modelling of OCM reactions over Mn/ $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst, *Fuel Process. Technol.* 115 (2013) 79–87.
- S. Arndt, T. Otremba, U. Simon, M. Yildiz, H. Schubert, R. Schomacker, Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ as catalyst for the oxidative coupling of methane. What is really known? *Appl. Catal. A Gen.* 425–426 (2012) 53–61.
- N.H. Othman, Z. Wu, K. Li, A micro-structured $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3.8}$ hollow fibre membrane reactor for oxidative coupling of methane, *J. Membr. Sci.* 468 (2014) 31–41.
- C. Karakaya, H. Zhu, C. Loebick, J.G. Weissman, R.J. Kee, A detailed reaction mechanism for oxidative coupling of methane over Mn/ $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst for non-isothermal conditions, *Catal. Today* 312 (2018) 10–22.
- M.R. Lee, M. Park, W. Jeon, J. Choi, Y. Suh, D.J. Suh, A kinetic model for the oxidative coupling of methane over $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$, *Fuel Process. Technol.* 96 (2012) 175–182.
- W. Liang, S. Sarsani, D. West, A. Mamedov, I. Lengyel, H. Perez, J. Lowrey, Performance improvement for a fixed bed reactor with layered loading catalysts of different catalytic properties for oxidative coupling of methane, *Catal. Today* 299 (2018) 60–66.
- A.M. Khan, K. Takanabe, M. Sarathy, A. Farooq, Kinetic Studies of Oxidative Coupling of Methane Reaction on Model Catalysts, Thesis, Chemical and Biological Engineering, KAUST department, physical sciences and engineering (PSE) division, Chemical and Biological Engineering Program, 2016.
- A. Malekzadeh, A.K. Dalai, A. Khodadadi, Y. Mortazavi, Structural features of $\text{Na}_2\text{WO}_4\text{-MO}_x/\text{SiO}_2$ catalysts in oxidative coupling of methane reaction, *Catal. Commun.* 9 (2008) 960–965.
- A. Palermo, J.P.H. Vazquez, A.F. Lee, M.S. Tikhov, R.M. Lambert, Critical influence of the amorphous silica-to-Cristobalite phase transition on the performance of Mn/ $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts for oxidative coupling of methane, *J. Catal.* 177 (1998) 259–266.
- B. Litawa, P. Michorczyk, J. Ogonowski, Influence of CO_2 on the catalytic performance of $\text{La}_2\text{O}_3/\text{CeO}_2$ and CaO/CeO_2 catalysts in the oxidative coupling of methane, *Polish J. Chem. Technol.* 15 (2013).
- S.J. Korf, J.A. Roos, J.W.H.C. Derksen, J.A. Vreeman, J.G.V. Ommen, J.R.H. Ross, Oxidative coupling of methane over Ba/CaO catalysts a comparison with Li/MgO, *Appl. Catal.* 59 (1990) 291–309.
- F. Cheng, J. Yang, L. Yan, J. Zhao, H. Zhao, H. Song, L. Chou, Effect of calcination temperature on characteristics and performance of solid acid WO_3/TiO_2 -supported lithium-manganese catalyst for the oxidative coupling of methane, *Eur. J. Inorg. Chem.* (2019).
- S. Lim, J.W. Choi, D.J. Suh, U. Lee, K.H. Song, J.M. Ha, Low-temperature oxidative coupling of methane using alkaline earth metal oxide-supported perovskites, *Catal. Today* 352 (2019) 127–133.
- M. Yildoz, U. Simon, T. Otremba, Y. Aksu, K. Kailasam, A. Thomas, R. Schomacker, S. Arndt, Support material variation for the Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst, *Catal. Today* 228 (2014) 5–14.
- N.S. Hayek, N.S. Lucas, C.W. Damouny, O.M. Gazit, Critical Surface parameters for the oxidative coupling of methane over the Mn-Na-W/SiO₂ catalyst, *ACS Appl. Mater. Interfaces* 8 (2017) 40404–40411.
- V. Fleischer, R. Steuer, S. Parishan, R. Schomacker, Investigation of the surface reaction network of the oxidative coupling of methane over $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalyst by temperature programmed and dynamic experiments, *J. Catal.* 341 (2016) 91–103.
- Somayeh Mahmoodi, M.Reza Ehsani, Marzieh Hamidzadeh, Effect of additives on Mn/SiO₂ based catalysts on oxidative coupling of methane, *J. Chem. Chem. Eng.* 30 (2011) 29–36.
- H.R. Godini, A. Gili, O. Gorke, S. Arndt, U. Simona Thomas, R. Schomaker, G. Wozny, Sol-gel method for synthesis of Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst for methanex oxidative coupling, *Catal. Today* 236 (2014) 12–22.
- R. Burch, G.D. Squire, S.C. Tsang, Role of chlorine in improving selectivity in the oxidative coupling of methane to ethylene, *Appl. Catal.* 46 (1989) 69–87.
- T.W. Elkins, H.E. Hagelin-Weaver, Characterization of Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ and Mn- $\text{Na}_2\text{WO}_4/\text{MgO}$ catalysts for the oxidative coupling of methane, *Appl. Catal. A Gen.* 497 (2015) 96–106.
- N. Hiyoshi, T. Ikeda, Oxidative coupling of methane over alkali chloride-Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts: Promoting effect of molten alkali chloride, *Fuel Process. Technol.* 133 (2015) 29–34.
- K.J. Yoon, S.W. Seo, Oxidative coupling of methane over sodium-salt-promoted zirconia catalysts prepared by the mixed solution method, *Appl. Catal. B Environ.* 7 (1996) 237–250.
- K.J. Yoon, H.L. Tung, Oxidative coupling of methane over sodium-chloride-promoted zirconia supported on sodium-preimpregnated silica, *Appl. Catal. A Gen.* 159 (1997) 59–74.
- Y. He, B. Yang, G. Cheng, On the oxidative coupling of methane with carbon dioxide over CeO_2/ZnO nanocatalysts, *Catal. Today* 98 (2004) 595–600.
- J. Kim, L.H. Park, J.M. Ha, E.D. Park, Oxidative Coupling of Methane over $\text{Mn}_2\text{O}_3\text{-Na}_2\text{WO}_4/\text{SiC}$ catalysts, *Catalysts* 9 (2019) 363.
- H. Liu, D. Yang, R. Gao, L. Chen, S. Zhang, X. Wang, A novel $\text{Na}_2\text{WO}_4\text{-Mn}/\text{SiC}$ monolithic foam catalyst with improved thermal properties for the oxidative coupling of methane, *Catal. Commun.* 9 (2008) 1302–1306.
- V. Tongnan, T. Sornchamni, N. Laosiripojana, U.W. Hartley, Study of crystal growth and kinetic parameters of Zn/ZnO oxidant in the presence of H_2O and CO_2 , *React. Kinet. Mech. Cat.* 125 (2018) 99–110.
- E. C. Scher, F. R. Zurcher, J. M. Cizeron, W. P. Schammel, A. Tkachenko, J. Gamoras, D. Karshedt, G. Nyce, Siluria Technologies, Inc., Nanowire Catalysts. United States patent US 2012/0041246 A1. 2012 Fed16.

- [33] L. Chou, Y. Cai, B. Zhang, J. Niu, S. Ji, S. Li, Influence of SnO₂-doped W-Mn/SiO₂ for oxidative conversion of methane to high hydrocarbons at elevated pressure, *Appl. Catal. A Gen.* 238 (2003) 185–191.
- [34] W. Zheng, D. Cheng, N. Zhu, F. Chen, X. Zhan, Studies on the structure and catalytic performance of S and P promoted Na-W-Mn-Zr/SiO₂ catalyst for oxidative coupling of methane, *J. Nat. Gas Chem.* 19 (2010) 15–20.
- [35] R.T. Yunarti, S. Gu, J. Choi, J. Jae, D.J. Suh, J. Ha, Oxidative coupling of methane using Mg/Ti-Doped SiO₂-supported Na₂WO₄/Mn catalysts, *ACS Sustain. Chem. Eng.* 5 (2017) 3667–3674.
- [36] N. Hiyoshi, K. Sato, Oxidative coupling of methane over Mn-Na₂WO₄/SiO₂ catalyst with continuous supply of alkali chloride vapor, *Fuel Process. Technol.* 151 (2016) 148–154.
- [37] H. Liu, X. Wang, D. Yang, R. Gao, Z. Wang, J. Yang, Scale up and stability test for oxidative coupling of methane over Na₂WO₄-Mn/SiO₂ catalyst in a 200 ml fixed-bed reactor, *J. Nat. Gas Chem.* 17 (2008) 59–63.
- [38] U. Zavyalova, M. Holena, R. Schlögl, M. Baerns, Statistical analysis of past catalytic data on oxidative methane coupling for new insights into the composition of high-performance catalysts, *ChemCatChem* 3 (2011) 1935–1947.
- [39] U.Z. Li, S. Wang, W. Hong, S. Zou, L. Xiao, J. Fan, Intelligent optimization of Na-Mn-W/SiO₂ for oxidative coupling of methane, *ChemNanoMat* 4 (2018) 5.
- [40] K. Otsuka, M. Hatano, T. Komatsu, Synthesis of C₂H₄ by partial oxidation of CH₄ over transition metal oxides with alkali-chlorides, *Stud. Surf. Sci. Catal.* 36 (1988) 383–387.
- [41] M. Daneshpayeh, A. Khodadadi, N. Mostoufi, Y. Mortazavi, R.S. Gharebagh, A. Talebizadeh, Kinetic modeling of oxidative coupling of methane over Mn/Na₂WO₄/SiO₂ catalyst, *Fuel Process. Technol.* 90 (2009) 403–410.
- [42] S. Parisha, P. Littlewood, A. Arinchtein, V. Fleischer, R. Schomacker, Chemical looping as a reactor concept for the oxidative coupling of methane over the Mn_xO_y-Na₂WO₄/SiO₂ catalyst, *Catal. Today* 311 (2018) 40–47.