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Changing the World's Energy Future

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Abstract

The structure and promotional effect of Mn in supported Mn-Na₂WO₄/SiO₂ catalysts for the oxidative coupling of methane (OCM) reaction has been debated for a longtime in the literature. In the current investigation, with the aid of multiple *in-situ* characterization studies, we show that the freshly calcined supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst possesses crystalline Na₂WO₄, Mn₂O₃ and SiO₂ (cristobalite phase) along with surface MnO_x and Na-WO_x sites at low temperature and oxidizing environments. Under the OCM reaction environment ($T > 800$ °C), the crystalline Na₂WO₄ phase melts and Mn₂O₃ phase reduces. In contrast, the surface MnO_x and Na-WO_x sites exhibit excellent thermal and chemical stability. Exposure of the 1.2Mn-5Na₂WO₄/SiO₂ catalyst to the OCM reaction environment redisperses the molten Na₂WO₄ phase on the SiO₂ support to form new surface WO_x sites. Interestingly, the stable MnO_x species interacts with both molten Na₂WO₄ phase and surface Na-WO_x sites during OCM reaction. Controlled transient kinetic experiments in TAP and detailed steady state OCM fixed-bed reaction studies reveal the role and promotional effect of Mn in the 1.2Mn-5Na₂WO₄/SiO₂ catalyst. The W-oxides (both molten Na₂WO₄ and surface Na-WO_x sites) are the active sites for the catalytic OCM reaction and the MnO_x species only function as promoters. The promotion of MnO_x strongly depends on the gas phase O₂ partial pressure and the MnO_x species act as mediators for oxygen exchange between the gas phase molecular O₂ and catalyst lattice oxygen. The temperature dependent MnO_x promotion reveals that the MnO_x species selectively promote the molten Na₂WO₄ phase at lower reaction temperature and the surface Na-WO_x sites at higher temperature.

Keywords

OCM

Mn-Na₂WO₄/SiO₂ catalyst

Active site

In-situ spectroscopy

In-situ Raman

TAP

Kinetics

Mn promotional effect

1. Introduction

The oxidative coupling of methane (OCM) is a single-step process for the conversion of CH_4 , the major component of natural gas, to value-added C_2 products (C_2H_6 and C_2H_4). Among the many catalysts tested for this reaction, the Na-promoted SiO_2 supported W-oxide based catalysts have been found very active, selective and stable for extended operation. [1], [2] The addition of MnO_x to supported $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts significantly improves the catalytic OCM performance. [3], [4], [5], [6] This has led to extensive investigations in the literature to understand the structure and promotion mechanism(s) of MnO_x .

The early studies on the structure of supported Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts employed only characterization studies under ambient and/or *ex-situ* conditions that were unable to provide relevant information regarding the nature of the catalytic active sites during the OCM reaction. [5], [6] Only recently, have *in-situ/operando* catalyst characterization studies been reported that are revealing the dynamic nature of the supported Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts as a function of environmental conditions. [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18] Both XRD and Raman showed that the crystalline α -cristobalite phase of the SiO_2 support in freshly calcined catalyst transforms to crystalline the β -cristobalite phase at elevated temperatures ($> \sim 250^\circ\text{C}$). [7], [8], [9], [10], [11], [12], [13], [15], [16], [17] The SiO_2 -supported Na_2WO_4 phase undergoes multiple phase transformations with temperature (crystalline cubic phase ($< 650^\circ\text{C}$) $\rightarrow$ crystalline orthorhombic phase ($650\text{--}750^\circ\text{C}$) $\rightarrow$ molten amorphous phase ($> 750^\circ\text{C}$)) as shown by XRD and Raman. [9], [13], [15], [16] The presence of MnO_x was found to increase the melting point of crystalline Na_2WO_4 by $\sim 30^\circ\text{C}$. [16] Furthermore, *in-situ* Raman studies revealed that the molten Na_2WO_4 phase is unstable at elevated temperatures ($> 700^\circ\text{C}$) and transforms to surface Na-coordinated WO_x (Na- WO_x) sites by dispersion on the SiO_2 support. [15] Additional studies showed that the surface Na- WO_x sites are thermally stable and catalytically active for the OCM reaction [12], [14], [15].

Although a general consensus has been reached in the literature regarding the stable structures of the SiO_2 support and Na-promoted WO_x phases under OCM relevant conditions, there is still ongoing debate regarding the stable structure(s) of the MnO_x phase. Only the crystalline Mn_2O_3 phase was detected by XRD in oxidizing environments. [7], [16] Complementary *in-situ* Raman studies also identified the crystalline α - Mn_2O_3 , γ - Mn_2O_3 , and $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$ (hausmanite) phases as present in oxidizing environment ($25\text{--}800^\circ\text{C}$). [16] Subsequent *in-situ* XRD analysis under the OCM reaction environment observed a significant reduction in the intensity or even the absence of the crystalline Mn_2O_3 phase [8], [11] and it was speculated that the Mn-oxide phase is either reduced or present as an amorphous phase during the OCM reaction. [11] A few other studies, however, observed the formation of the crystalline MnWO_4 phase after melting of Na_2WO_4 or under an OCM reaction environment with a high CH_4/O_2 ratio. [9], [10] The crystalline $\text{Mn}_7\text{SiO}_{12}$ phase has also been reported to be present for supported Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts below $\sim 650^\circ\text{C}$. [13] At higher temperatures and OCM reaction environment, the crystalline $\text{Mn}_7\text{SiO}_{12}$ phase was reported to disappear along with the melting of Na_2WO_4 phase with concomitant appearance of the crystalline

MnWO₄ phase. The lack of consensus in the literature regarding the stable structure of the MnO_x phase warrants additional molecular level investigation *via in-situ /operando* spectroscopic characterization.

Different opinions are also seen in the literature regarding the role of the MnO_x phase (catalytic active site for OCM *vs.* promoter) and its promotional effect on the W-oxide phases during the OCM reaction. In a few reports, the (distorted) WO₄ site present in the crystalline Na₂WO₄ lattice was proposed to be the active site for the OCM reaction over supported Mn-Na₂WO₄/SiO₂ catalysts, and Mn-oxide was reported to participate in oxygen spillover to the W-oxide centers. [3], [19], [20], [21], [22], [23] It was also reported that the bulk MnO₄ and MnO₆ oxide centers are responsible for both CH₄ and O₂ activation, respectively. [24] The second proposal regarding the role of Mn raises the question as to the role of the W-oxide phase for the OCM reaction. The oxygen in the bridging Na-O-Mn bond was also proposed as the active site because of the similar catalytic performances for Mn-Na₂WO₄/SiO₂, Mn-Na₂WO₄/MgO and NaMnO₄/MgO catalysts. [25] Both oxygen atoms on the bridging Na-O-Mn and Na-O-W were proposed as active sites in another study because of the substantial role of all three active metal oxides in the Mn-Na₂WO₄/SiO₂ catalyst system. [26] For the same reason, the interface between crystalline Mn₂O₃ and Na₂WO₄ phases was also speculated to be the active site. [27] The crystalline Mn₂O₃ phase was also proposed to be an active site because of its excellent redox behavior. [7] Furthermore, a recent DFT study emphasized that surface Mn oxo sites present on the Mn₂O₃ crystal as the active site for the CH₄ activation due to the higher energy barrier associated with the W oxo sites. [28] In contrast, oligomeric MnO_x, Mn-WO₃ and MnWO₄ phases of Mn-oxides present in the supported Mn-Na-WO_x/SiO₂ catalysts (with low Na loadings to avoid formation of crystalline Na₂WO₄ phase) were not found to contribute towards the OCM reaction chemistry. [14] Additionally, the Mn-oxide has also been proposed to function as a promoter for the low temperature OCM reaction. [29] In summary, there is no consensus regarding the role and promotional effect of Mn-oxide towards the OCM reaction over supported Mn-Na₂WO₄/SiO₂.

The involvement of lattice oxygen species in the supported Mn-Na₂WO₄/SiO₂ catalysts for CH₄ activation and oxidation is also considered paramount in the OCM literature. [13], [17], [30], [31], [32], [33], [34] These studies, however, did not undertake detailed investigation into the nature and origin of active lattice oxygen species and/or their roles in the OCM reaction network. [35] Recent *in-situ* spectroscopic and transient kinetic investigations showed that the supported Na₂WO₄/SiO₂ catalysts possess two different types of oxygen species: (i) atomic O species associated with the surface Na-WO_x sites primarily responsible for formation of C₂ products, and (ii) dioxygen O₂ species originating from the molten Na₂WO₄ phase involved in the production of CO₂ and oxidative dehydrogenation of C₂H₆. [15], [35] The addition of MnO_x to the supported Na₂WO₄/SiO₂ catalysts was shown to improve the total amount and release rate of O₂ species associated with the molten Na₂WO₄ phase. Furthermore, the addition of MnO_x was found to improve the C₂ product selectivity. [35] Despite these significant findings, several important points still need further clarification: (i) is the MnO_x phase by itself active towards OCM? if so, then how selective is that activation step? (ii) does MnO_x act as the active center or just play the role of promoter in supported Mn-Na₂WO₄/SiO₂ catalysts? (iii) how does the promotion effect of MnO_x vary with reaction conditions (temperature, gas-space velocities, long-term catalyst stability, *etc.*)? (iv) how does MnO_x change the reaction chemistry of the Na₂WO₄/SiO₂ catalyst?

The current investigation, with the aid of multiple *in-situ* characterization techniques (Raman spectroscopy, XRD, NAP-XPS (near ambient pressure X-ray photoelectron spectroscopy)), aims at revealing the stable structure of the MnO_x phase in supported $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts during the OCM reaction. Additionally, with the aid of H_2 -TPR (temperature programmed reduction), controlled transient reaction studies in TAP (temporal analysis of products) and detailed steady state fixed-bed reactor kinetic studies, we aim at resolving the roles and promotional effect of MnO_x in supported $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts towards the OCM reaction network.

2. Experimental

2.1. Catalyst Synthesis

The catalysts were synthesized using the incipient wetness impregnation (IWI) method. At first, the SiO_2 support (Cabot CAB-O-SIL® EH5) was treated with water and crushed into a fine powder (100–150 μm particle size), as described previously. [15] The required amount of aqueous solution of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was impregnated into the water-treated SiO_2 support, followed by overnight drying at room temperature. Subsequently, an aqueous $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ solution of the required amount was impregnated into the above sample and was again dried overnight at room temperature. The above sample was further dried at 120 °C for 2 h, and finally calcined at 800 °C for 8 h, under flowing air. For the preparation of $\text{Na}_2\text{WO}_4/\text{SiO}_2$ and Mn/SiO_2 catalysts only the desired metal oxide precursor was incorporated into the SiO_2 support, and the drying and calcination steps followed were similar to as described above. The catalysts were named according to the weight loadings of the active metal/metal-oxide components. For example, the supported 1.2Mn-5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst contains 1.2 % of Mn and 5 % of Na_2WO_4 on weight basis.

The powder sample (100–150 μm particle size), as received after the calcination step is used for *in-situ* Raman and H_2 -TPR experiments. For *in-situ* XRD and NAP-XPS studies the powder sample was pressed to form a thin disk. For TAP and steady-state kinetic studies, the powder samples were pressed to form pellets and then crushed to obtain 250–300 μm size particles.

2.2. *In-situ* XRD

The powder X-Ray diffraction (XRD) was recorded by a Bruker-AXS D5005 (Bruker, Billerica, MA, USA) with a $\text{Co K}\alpha$ source. For the experiment, the sample was first pressed to form a disk, which was then mounted on a gold foil before placing it on the heater plate. Then the sample temperature was increased to 400 °C (at 10 °C/min), under constant flow (~ 50 cc/min) of dry air. After the dehydration of the sample at 400 °C for 1 h, the XRD spectrum was collected. Following that, the sample was heated to 900 °C (at 10 °C/min), in the same gas environment, and another spectrum was collected. Before the analysis of the XRD data, the signal from the gold foil was subtracted.

2.3. *In-situ* Raman spectroscopy

For the collection of *in-situ* Raman spectra of the sample in different environmental conditions, the Horiba-Jobin Yvon LabRam HR instrument was utilized. The details of the instrument is

described elsewhere. [12] In the current investigation, approximately 25–30 mg of the sample (in powder form) was loaded in the sample cup of the Linkam CCR 1000 environmental cell with a quartz window and O-ring seal. For all spectra collection, the 532 nm laser was utilized.

At first, the sample was dehydrated at 400 °C under flowing 10 % O₂/Ar (~30 cc/min) for 1 h. Subsequently, a dehydrated spectrum was collected at 400 °C. The sample was then heated to 900 °C (at 10 °C/min), followed by another spectrum collection. Then the gas environment was switched to the OCM conditions (CH₄:O₂:N₂ 3.3:1:4, total flow ~65 cc/min). After treatment of the sample at 900 °C for 2 h, in the OCM gas mixture, another spectrum was collected. The sample was cooled down in the same OCM gas flow to enhance the spectral resolution and avoid thermal broadening, and two more spectra were collected at 400 °C and 120 °C.

2.4. H₂-TPR

The H₂-TPR experiments were conducted in a Micromeritics® AutoChem II instrument equipped with a TCD detector. For each experiment, about 100 mg of the catalyst sample was used. For H₂-TPR of freshly calcined catalysts, the catalyst samples were first dehydrated in 10 % O₂/Ar (~30 cc/min) at 400 °C for 1 h, then cooled down to 100 °C, followed by flushing with pure Ar (~30 cc/min) for 30 mins. To conduct H₂-TPR on the OCM reaction mixture treated catalyst, the sample was first dehydrated at 400 °C under flowing 10 % O₂/Ar (~30 cc/min) for 1 h, followed by heating to 900 °C. At 900 °C, the gas environment was switched to CH₄ + O₂ + N₂ (3.3:1:4, total flow ~65 cc/min), and the sample was conditioned for 2 h. Subsequently, the sample was cooled down to 100 °C, followed by flushing with Ar (~30 cc/min) for 30 mins. After the pre-treatment steps, the H₂-TPR experiments were then performed by ramping the temperature of the catalyst bed in 10 % H₂/Ar (30 cc/min) at a rate of 10 °C/min from 100° to 1000 °C.

For the cyclic H₂-TPR experiment, the reduced samples were reoxidized *in-situ* at 900 °C, in the flow of OCM gas mixture (CH₄ + O₂ + N₂ 3.3:1:4, total flow ~65 cc/min) for 2 h. Subsequently, the sample was cooled down to 100 °C, followed by flushing with Ar (~30 cc/min) for 30 mins. Finally, the H₂-TPR experiment was performed on the reoxidized catalysts as described above. The number of lattice O-atoms removed for each TPR experiment was calculated by finding the area under the respective TPR profiles and calibrating against the reduction profile of known amounts of CuO standard [36] (see Fig. S2 and associated details).

2.5. TAP experiments

The transient kinetic experiments were conducted in a TAP 3 instrument, Mithra Technologies. Three different types of TAP pump-probe experiments were conducted in this study. For these experiments, 50 % O₂/He, 50 % ¹³CH₄/Ar, 50 % C₂H₆/Ar and 50 % C₂H₄/Ar gases were utilized. The details of the reaction gas mixture procurement and blending procedures are described elsewhere. [15].

Approximately 25 mg of the catalyst sample was loaded into a quartz micro-reactor (I.D. 4 mm, Length 38 mm) between inert quartz particles of size 250–300 µm. Next, the catalyst bed was evacuated to ~ 4 × 10⁻⁶ Pa, followed by heating to 800 °C (10 °C/min), with continuous pulsing of O₂/He and held at 800 °C for 30 mins. After pretreatment of the catalyst samples, pump-probe experiments were conducted according to the details below. In each case, the pump-probe spacing

between the O₂/He and ¹³CH₄/Ar (or C₂H₆/Ar or C₂H₄/Ar) gas was maintained at 2 s. This ensures complete removal of gas-phase O₂ before the introduction of reactant gas into the catalyst bed. Thus, the products obtained in these experiments are not influenced by any gas phase oxygen pulse associated with the pump pulse. The detection of different gases was conducted using a mass-spectrometer (SRS RGA 200), situated at the exit of the micro-reactor. Also, in each case, calibration gas mixtures were utilized to determine the mass fragmentation pattern of each reactant and product gas for deconvolution of the overlapping masses. All pump-probe experiments were conducted outside the Knudsen diffusion regime. For each experiment, data were presented by taking average of 15–25 pulse responses. The product yields of different catalysts were normalized by the respective BET surface area for fair comparison.

- O₂-¹³CH₄ pump-probe experiments

¹³CH₄ isotope gas was utilized to better distinguish CO and C₂ products. For these experiments, the O₂/He and ¹³CH₄/Ar pulse sizes were approximately maintained $\sim (2.15 \pm 0.05) \times 10^{-8}$ moles/pulse and $(8.75 \pm 0.05) \times 10^{-8}$ moles/pulse, respectively. For species identification, *m/z* of 40 (*Ar*); 17 (¹³CH₄); 29 (¹³CO); 30 (¹³C₂H₆); 32 (O₂) and 45 (¹³CO₂) were utilized.

- O₂-C₂H₆ and O₂-C₂H₄ pump-probe experiments

For O₂-C₂H₆ pump-probe experiments, O₂/He and C₂H₆/Ar pulse sizes were approximately maintained $\sim (3.25 \pm 0.05) \times 10^{-9}$ moles/pulse and $(3.25 \pm 0.05) \times 10^{-8}$ moles/pulse, respectively, and *m/z* values of 40 (*Ar*); 26 (C₂H₄); 28 (CO); 30 (C₂H₆); 32 (O₂) and 44 (CO₂) were utilized for species identification. For the O₂-C₂H₄ pump-probe experiment, O₂/He and ¹³CH₄/Ar pulse sizes were approximately maintained $\sim (4.2 \pm 0.1) \times 10^{-9}$ moles/pulse and $(4.1 \pm 0.1) \times 10^{-8}$ moles/pulse, respectively and *m/z* values of 40 (*Ar*); 26 (C₂H₄); 28 (CO); 32 (O₂) and 44 (CO₂) were utilized for species identification.

2.6. Steady state experiments

Steady-state OCM reaction studies were conducted in a tubular fixed-bed quartz reactor (I.D. 6 mm and half-length 180 mm). A quartz frit was located at the middle of the tube. For each experiment, approximately 100 mg of catalyst sample was loaded onto the quartz frit. Then the remaining empty space inside the tube was filled with quartz beads (500–700 μm) to minimize the contribution from gas-phase reactions. The loaded tube was then placed in a programmable electric furnace. The temperature of the catalyst bed was monitored by a thermocouple (secured inside a quartz thermowell) placed directly above the catalyst bed.

Prior to any reaction, the catalyst sample was first heated to the desired reaction temperature (750, 775 or 800 °C) at a rate of 10 °C/min, under a flowing O₂ (~ 10 cc/min) and N₂ (~ 40 cc/min) gas mixture and held at the reaction temperature for ~ 30 min. Then the reactant gas mixture, CH₄, O₂, diluted in N₂, was introduced (at different ratios and space velocities) into the reactor. The reaction was maintained at each condition for ~ 3 h to ensure that steady-state conditions were achieved. The water vapor produced during the reaction was removed by cooling the exit gas mixture in a condenser at 0 °C. Gases were analyzed using online gas chromatography (GC System 2010, Shimadzu Technology), equipped with a flame ionization detector (GC-FID) and two thermal conductivity detectors (GC-TCD1 and GC-TCD2). The GC-TCD1 detector was equipped with Carboxen® 1010 PLOT (SUPLECO Analytical, Catalogue number 25467) fused silica capillary

column to separate CO₂, C₂H₂, C₂H₄ and C₂H₆. The GC-TCD2 detector is equipped with HP-PLOT Molesieve column (Agilent J&W GC Columns, Part number 19095 P-MSO) to separate O₂, N₂, CH₄ and CO. Both GC-TCD1 and GC-TCD2 detectors use He as carrier gas. The GC calibration was done using calibration gas mixtures in a 5-point calibration method. For data analysis, an average of 5–6 data points were utilized in each case.

CH₄, O₂ conversion and CO, CO₂, C₂H₆ and C₂H₄ selectivity and yield values were obtained by the following formulae ((1), (2), (3)):

$$\% \text{ Conversion} = \frac{(F_i - F_o)}{F_i} \times 100 \quad (1)$$

where, F_i and F_o are the inlet and outlet molar flow rates (mol/s), respectively, of CH₄ or O₂.

$$\% \text{ Selectivity}_j = \frac{n_{C_j}}{\sum n_{C_j}} \times 100 \quad (2)$$

where, n_{C_j} is the number of moles of carbon atoms in product j .

$$\% \text{ Yield}_j = \frac{\% \text{ CH}_4 \text{ Conversion} \times \% \text{ Selectivity}_j}{100} \quad (3)$$

3. Results

3.1. Mn loading for optimum OCM catalytic performance

The general consensus in the OCM literature is that 2 wt % Mn loading is optimum for giving the highest catalytic OCM performance of supported Mn-5Na₂WO₄/SiO₂ catalysts, although the Mn loading between 0.5 and 3 wt % (on metal basis) can be considered the best. [5] The very first publication that systematically studied the effect of active metal oxide phases found 1 wt % Mn loading gave the best OCM performance. [26] Subsequently, another study reported the 2 wt % Mn loading to have the highest OCM activity. [37] The large variation in the optimum Mn loading can be attributed to the catalyst synthesis approach and/or parameters utilized for conducting the reaction studies. This observation compelled us to explore different Mn loadings for our supported Mn-5Na₂WO₄/SiO₂ catalysts.

Supported Mn-5Na₂WO₄/SiO₂ catalysts with three different Mn loadings (1.2, 2 and 3.5 wt %) were prepared. The corresponding BET surface area and catalytic performance are presented in Table S1, Table S2 and Fig. 1. All catalysts possess similar surface areas (~3–4 m²/g). The addition of a small amount of Mn (1.2 wt %) increases the CH₄ activity and C₂ product selectivity of supported 5Na₂WO₄/SiO₂ catalyst by 35–40 %. The addition of higher amounts of Mn (2 and 3.5 wt %), however, does not significantly improve the catalytic OCM performance. Thus, for the current investigation the 1.2Mn-5Na₂WO₄/SiO₂ catalyst was chosen as the representative catalyst to study the role and promotional effect of Mn. The performance of 5Na₂WO₄/SiO₂ and 1.2Mn/SiO₂ catalysts will be discussed as needed for better understanding of the Mn promotional effect.

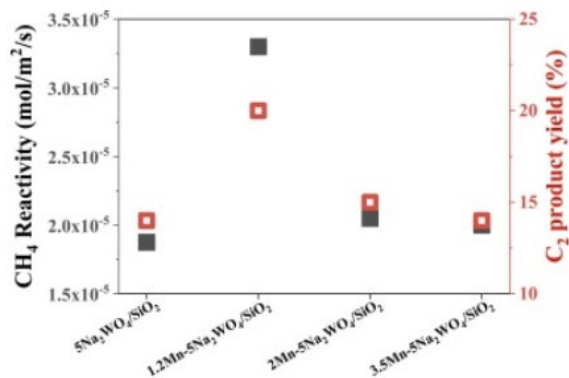


Fig. 1. The CH₄ reactivity (mol/m² cat/s) obtained from steady-state OCM experiments over supported Mn-Na₂WO₄/SiO₂ catalysts. Reaction temperature 800 °C, gas space velocity 48 L/g cat/h and CH₄:O₂:N₂ 50:15:35. The corresponding CH₄ conversion and product selectivity values are shown in Table S2.

3.2. In-situ XRD

The *in-situ* XRD spectra of the supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst are presented in Fig. 2. The spectrum of the dehydrated catalyst at 400 °C shows the presence of the crystalline Na₂WO₄, Mn₂O₃ and β-cristobalite (SiO₂) phases. Upon increasing the temperature to 900 °C, only the crystalline Mn₂O₃ and the β-cristobalite (SiO₂) phases are observed, and the Na₂WO₄ crystalline phase is no longer detected.

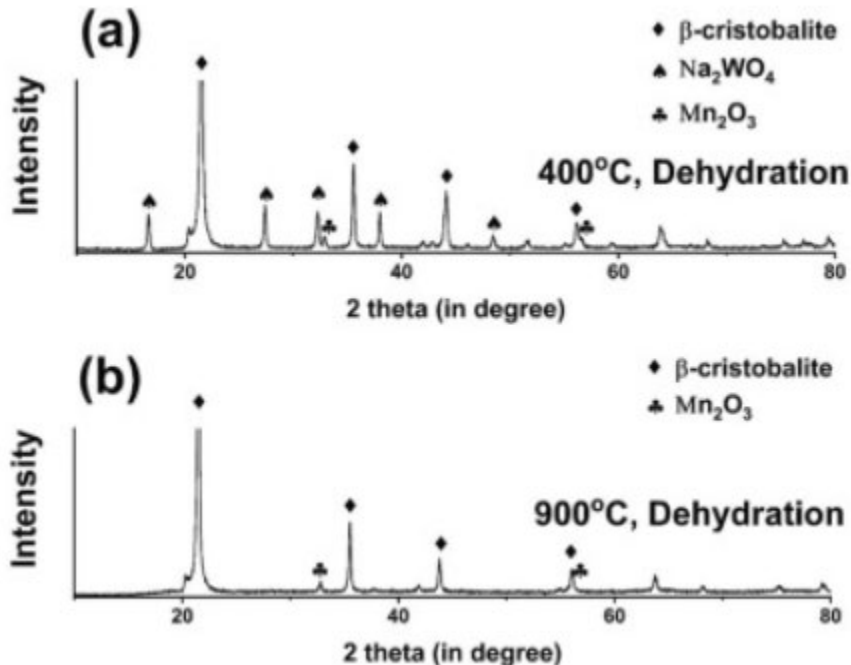


Fig. 2. *In-situ* XRD spectra of 1.2Mn-5Na₂WO₄/SiO₂ catalyst under dehydrated conditions at (a) 400 °C and (b) 900 °C.

3.3. In-situ Raman spectroscopy

In-situ Raman experiments were conducted to complement the *in-situ* XRD findings (*i.e.*, to identify oxide phases lacking long range order and small NPs (<3 nm in size)) to fully understand the structural dynamics of the supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst in oxidizing and OCM reaction environments (see Fig. 3).

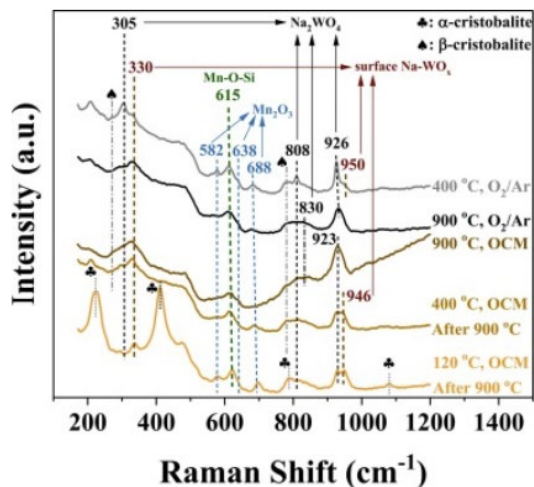


Fig. 3. *In-situ* Raman spectra of supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst in different environmental conditions.

3.3.1. In-situ Raman spectra in oxidizing environments

The Raman spectrum of the dehydrated 1.2Mn-5Na₂WO₄/SiO₂ catalyst at 400 °C (in O₂/Ar environment) exhibits three bands at 926, 808 and 305 cm⁻¹ associated with the vibrations of the crystalline Na₂WO₄ phase. [13], [15], [16], [38] The Raman bands at 582, 638 and 688 cm⁻¹ arise from the vibrations of the Mn₂O₃ crystalline phase. [39], [40] Apart from the crystalline phases, two more Raman vibrations at 950 and 330 cm⁻¹ are present from surface Na-WO_x sites. [12], [14], [15], [41] Another strong band is observed ~615 cm⁻¹ that is absent for the Mn-free supported 5Na₂WO₄/SiO₂ catalyst, [12], [15] which indicates it originates from the presence of Mn-oxide. This vibration does not match with any of the crystalline Mn-oxide phases or the crystalline MnWO₄ phase. [39], [42] The band at ~615 cm⁻¹ is also quite different and far more intense than the vibration from the SiO₂ defect mode. [43] Based on these comparisons, the Raman band at ~615 cm⁻¹ is assigned to the vibration of the Mn-O-Si bond from surface MnO_x species on the SiO₂ support. A similar vibrational band has been observed from Raman spectroscopy of supported MnO_x/SiO₂ catalysts. [14], [44].

Further heating the catalyst to 900 °C in an O₂/Ar environment results in disappearance of the 808 and 305 cm⁻¹ bands of crystalline Na₂WO₄, whereas the intensity of the 926 cm⁻¹ band from crystalline Na₂WO₄ is observed to decrease with noticeable broadening. A new band at

~830 cm⁻¹ also appears, which is from asymmetric W-O vibration of the molten Na₂WO₄ phase. [45] In contrast, Raman vibrations from the surface Na-WO_x sites (330 cm⁻¹ and ~946 cm⁻¹, shoulder of 926 cm⁻¹ band), crystalline Mn₂O₃ (582, 638 and 688 cm⁻¹), and Mn-O-Si

(615 cm^{-1}) are present at 900 $^{\circ}\text{C}$ in the oxidizing environment, although with noticeable thermal broadening.

3.3.2. In-situ Raman spectra in an OCM environment

Switching the gas flow to an OCM reaction mixture at 900 $^{\circ}\text{C}$ results in complete disappearance of the Raman vibrations from the crystalline Mn_2O_3 phase (582, 638 and 688 cm^{-1}), but the Raman vibrations from the surface Na-WO_x sites (330 cm^{-1} and $\sim 946 \text{ cm}^{-1}$) and surface Mn-O-Si sites (615 cm^{-1}) remain at 900 $^{\circ}\text{C}$ under the OCM environment.

Upon cooling to lower temperatures (400 $^{\circ}\text{C}$ and then to 120 $^{\circ}\text{C}$ in the OCM gas mixture), the Raman bands from the crystalline Na_2WO_4 and Mn_2O_3 phases reappear with the Raman bands shifting from 926 to 923 cm^{-1} and 950–946 cm^{-1} . Additionally, the relative intensity of Raman bands from the crystalline Na_2WO_4 phase (923 and 305 cm^{-1}) significantly decreases in comparison to the Raman vibrations from the surface Na-WO_x sites (946 and 330 cm^{-1} , respectively) after treatment under the OCM reaction conditions. No change in the Mn-O-Si vibration at 615 cm^{-1} is noticed. The crystalline β - to α -cristobalite phase transformation of the SiO_2 support is also observed for the 400 and 120 $^{\circ}\text{C}$ spectra, respectively.

3.4. H_2 -TPR

The H_2 -TPR spectra of freshly dehydrated and OCM reaction treated supported 1.2Mn-5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts are shown in Fig. S3 and Fig. 4. To understand the effect of MnO_x promotion, the corresponding H_2 -TPR data obtained for the 5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts are also included for comparison.

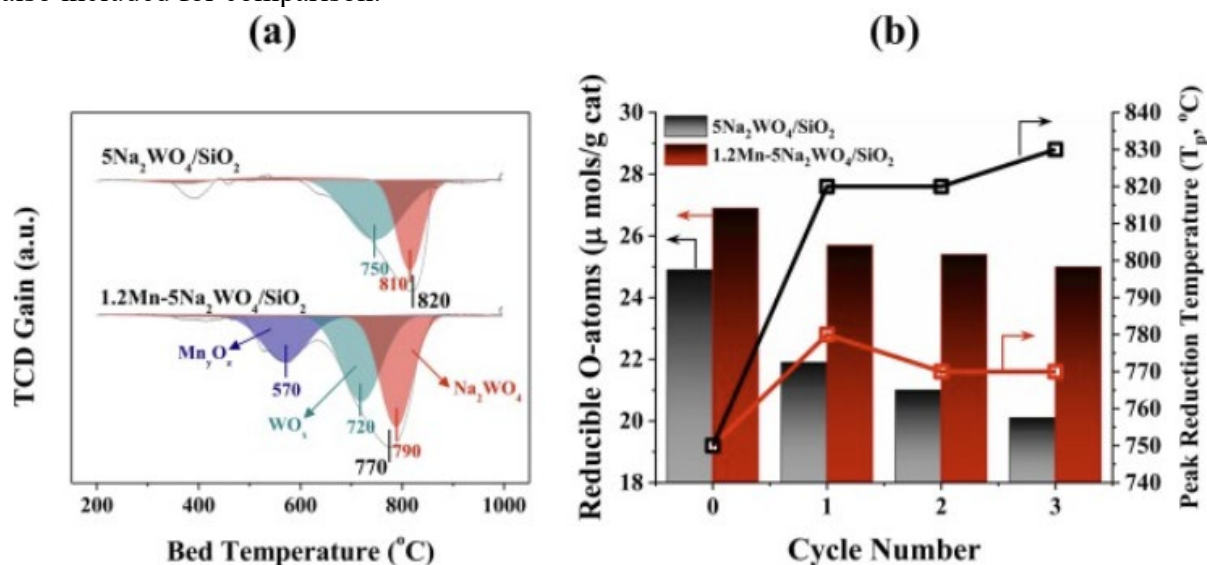


Fig. 4. (a) H_2 -TPR profiles of supported 5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ and the 1.2Mn-5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts after treatment in OCM reaction conditions. (b) Quantified lattice O-atoms removed and peak reduction temperatures (associated with only the reduction of W-oxide phases: surface Na-WO_x and Na_2WO_4) for freshly calcined (Cycle Number 0), OCM reaction mixture treated (Cycle

Number 1) and reoxidized (Cycle Number 2 and 3) supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ and the supported $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts.

Supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst: The H_2 -TPR of the freshly calcined supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst exhibits a peak $\sim 750^\circ\text{C}$ (see Fig. S3). After treatment in OCM reaction conditions, the reduction peak shifts to a higher temperature ($\sim 820^\circ\text{C}$). A better analysis of reduction from different oxide phases is presented in Fig. 4(a). Two distinct reduction regimes can be observed for the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst. The surface $\text{Na}-\text{WO}_x$ sites (green highlighted area) reduce at a lower temperature than the corresponding Na_2WO_4 NPs (red highlighted area). [12], [15] The lattice O-atoms removed, along with the corresponding reduction peak temperatures for freshly calcined, OCM reaction mixture treated and *in-situ* reoxidized supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts are shown in Fig. 4(b). The peak reduction temperature increases and the amount of lattice O-atoms modestly decreases: freshly calcined (750°C , $\sim 25 \mu\text{mol/g cat}$) $\rightarrow$ OCM reaction mixture treated (820°C , $< 22 \mu\text{mol/g cat}$) $\rightarrow$ *in-situ* reoxidized (830°C , $< 20 \mu\text{mol/g cat}$) $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts.

Supported $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst: The reduction peak for the freshly calcined $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst is $\sim 750^\circ\text{C}$, which demonstrated a minor increase towards higher temperature ($\sim 770^\circ\text{C}$) after treatment in the OCM reaction mixture (see Fig. S3). Similar to the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst, two separate reduction regimes, from surface $\text{Na}-\text{WO}_x$ sites and Na_2WO_4 NPs, are present for the supported $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts at higher temperatures (see Fig. 4(a)). An additional reduction peak is present at $\sim 570^\circ\text{C}$ that is assigned to the reduction of surface MnO_x species. [46], [47] The peak reduction temperature (from 750° to 770°C) and removable lattice O-atoms (from 27 to $25 \mu\text{mol/g cat}$, $\sim 7\%$ change) change (slightly increase and decrease, respectively) in going from freshly calcined $\rightarrow$ OCM reaction mixture treated $\rightarrow$ *in-situ* reoxidized supported $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts (see Fig. 4(b)).

3.5. TAP studies

TAP pump-probe experiments were conducted over the $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ and $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts to understand the promotional effect of MnO_x on the OCM surface reaction network. It has been previously shown that the molten Na_2WO_4 phase in $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst possesses dissolved molecular oxygen species at OCM relevant temperature which desorbs with the introduction of a secondary probe pulse. [15], [35] Furthermore, the amount of molecular dioxygen released from the $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst increases in the presence of MnO_x species. [35] In agreement with this finding, a higher amount of dioxygen release, during the probe pulse, was found for the supported $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst for all pump-probe experiments (see Fig. 5).

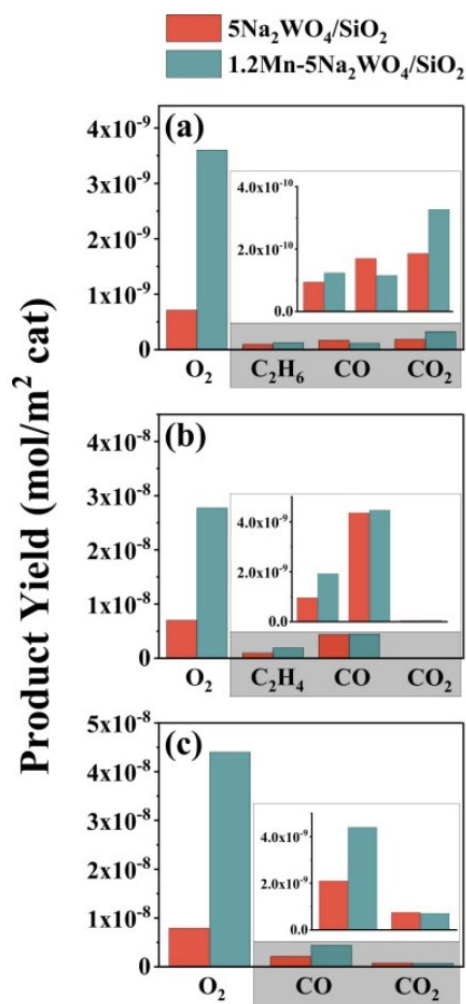


Fig. 5. Product formation associated with the secondary (probe) pulse of TAP. a) $\text{O}_2\text{-}^{13}\text{CH}_4$, b) $\text{O}_2\text{-C}_2\text{H}_6$ and c) $\text{O}_2\text{-C}_2\text{H}_4$ pump-probe experiments in the non-Knudsen diffusion regime for supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ and $1.2\text{Mn-}5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts at 800°C . The inset in each plot shows the enlarged version of the highlighted sections in the respective plots. The carbon balance, hydrocarbon conversion and C_2 selectivity for all pump-probe experiments are reported in Table S3.

For the $\text{O}_2\text{-}^{13}\text{CH}_4$ pump-probe experiment, the addition of MnO_x only results in a slight change in formation of C_2H_6 (slightly increased) and CO (slightly decreased). In contrast, a significant increase ($\sim 40\%$) in the yield of CO_2 is noticed after MnO_x addition (see Fig. 5(a)). For the $\text{O}_2\text{-C}_2\text{H}_6$ pump-probe experiment, MnO_x addition does not change the yield of CO and CO_2 . In contrast, the C_2H_4 yield almost doubles due to MnO_x promotion. Finally, for $\text{O}_2\text{-C}_2\text{H}_4$ pump-probe experiment, MnO_x addition increases the CO formation and does not affect the CO_2 yield.

3.6. Steady state reaction studies

Steady state OCM reaction studies were carried out to complement the transient TAP experimental findings in order to gain additional insights into the role and promotion of MnO_x species for the OCM reaction. (see Table 1, Fig. 6 and Fig. 7).

Table 1. Steady state OCM performance of multiple supported catalysts and quartz bed at 800 °C, $\text{CH}_4:\text{O}_2:\text{N}_2$ 50:15:35. The gas-space velocities are mentioned in the table.

Gas-space Velocity (L/g cat/h)	CH_4 conversion (%)	C_2 selectivity (%)	$\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ yield ratio
1.2 Mn/SiO₂			
120	12.1	50	0.7
72	14.1	48	1
48	16.2	45	1.4
5Na₂WO₄/SiO₂			
120	14.6	69	0.85
72	21.6	59	1.5
48	24.8	57	2.4
1.2Mn-5Na₂WO₄/SiO₂			
120	14.8	72	1
72	28.5	61	3.1
48	34.9	58	5.4
Quartz bed			
120	2.6	78	0.28
72	3.3	71	0.48
48	6.8	62	1.1

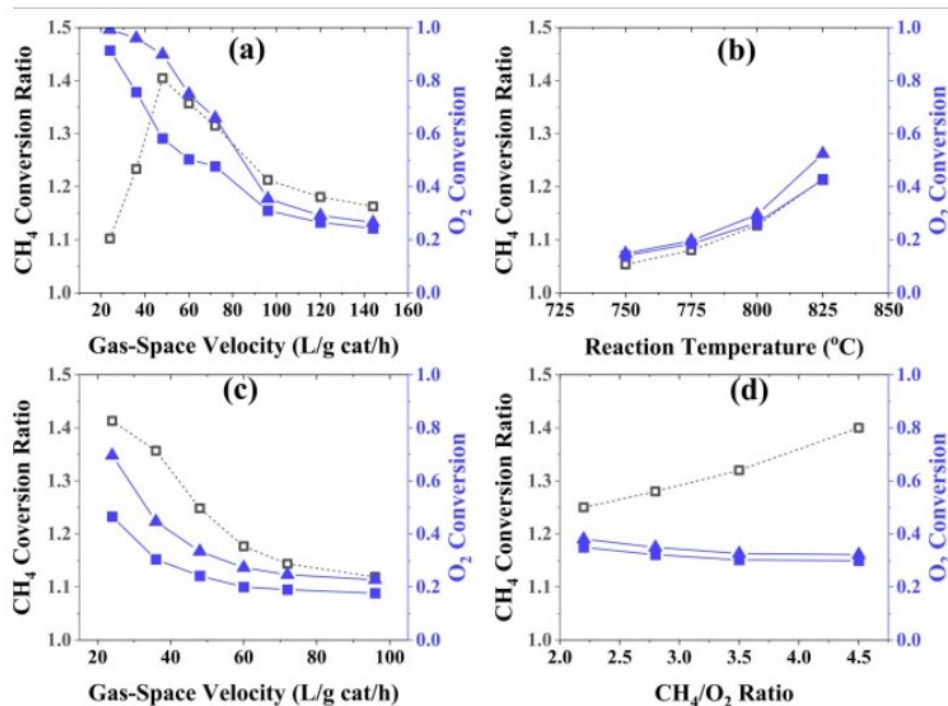


Fig. 6. The CH₄ Conversion Ratio of 1.2Mn-5NaWO₄/SiO₂ to 5NaWO₄/SiO₂ catalyst (empty black square) is shown for different reaction conditions, (a) 800 °C, varying gas-space velocity, CH₄:O₂:N₂ 50:15:35, (b) varying reaction temperature at a fixed gas-space velocity of 72 L/g cat/h, CH₄:O₂:N₂ 50:15:35, (c) 750 °C, varying gas-space velocity, CH₄:O₂:N₂ 50:15:35, and (d) 800 °C, gas-space velocity 60 L/g cat/h, varying CH₄/O₂ ratio at a fixed CH₄ partial pressure of 0.3. The corresponding O₂ Conversion for 1.2Mn-5NaWO₄/SiO₂ (solid blue triangle) and 5NaWO₄/SiO₂ (solid blue square) catalysts are also shown in the figure.

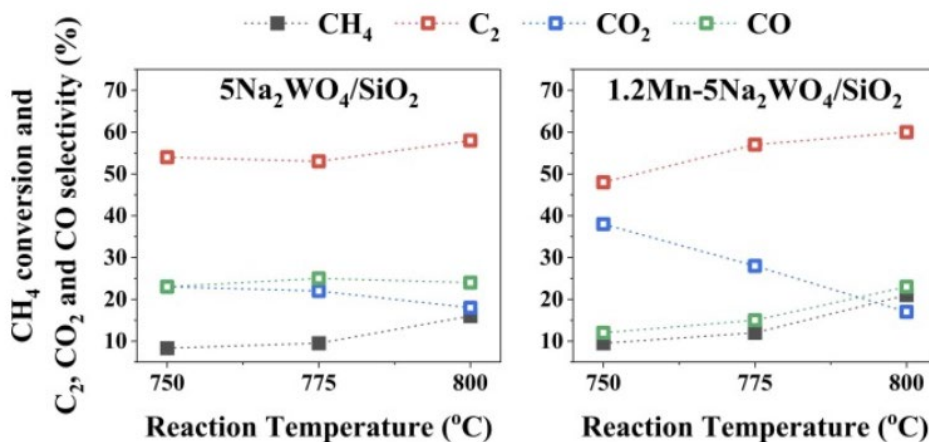


Fig. 7. The CH₄ conversion, and C₂, CO₂ and CO selectivity of 5Na₂WO₄/SiO₂ and 1.2Mn-5Na₂WO₄/SiO₂ catalysts at varying reaction temperature at a fixed gas-space velocity of 72 L/g cat/h, CH₄:O₂:N₂ 50:15:35.

The supported $1.2\text{MnO}_x/\text{SiO}_2$ catalyst is active for the OCM reaction, but yields low C_2 selectivity (Table 1). The supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst exhibits higher activity and C_2 product selectivity than the supported $1.2\text{Mn}/\text{SiO}_2$ catalyst, especially for low gas-space velocities. The addition of Mn to the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst ($1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst) significantly improves the CH_4 activity without compromising the C_2 selectivity and also increases the ratio of $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ($1.2\text{Mn}/\text{SiO}_2 < 5\text{Na}_2\text{WO}_4/\text{SiO}_2 < 1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$).

The effect of MnO_x on the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst for CH_4 activity and product selectivity is a strong function of the reaction conditions (see Table 1). Steady state OCM reactions over the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ and $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts were conducted over a wide range of experimental conditions (gas-space velocity, temperature, and CH_4/O_2 ratio) in order to gain deeper insight and the results are presented in Fig. 6. For better quantitative understanding, the effect of MnO_x is presented as the CH_4 conversion ratio of the $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ to $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts. The respective O_2 conversion of these catalysts are also included in the Fig. 6.

Initially, the space velocity was varied at a fixed reaction temperature (800°C , see Fig. 6(a)). The effect of Mn becomes more pronounced (the CH_4 conversion ratio increases) up to a certain point and then decreases with decreasing space velocity. To understand this influence of Mn promotion behavior, the corresponding O_2 conversion values were compared, and the observations can be summarized as follows:

- (i)
At low O_2 conversion values (high gas space velocities), sufficient gas-phase O_2 is available for CH_4 conversion and, consequently, MnO_x promotion does not significantly affect the CH_4 conversion (conversion ratio is smaller).
- (ii)
As the gas space velocity is progressively lowered, the conversion values of the reactants increase and the availability of gas phase O_2 diminishes. Under these conditions, the promotion by MnO_x becomes more pronounced.
- (iii)
As the gas space velocity is further lowered (the lowest two values in Fig. 6(a)), the CH_4 conversion ratio decreases because the O_2 conversion for the promoted supported $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst approaches almost 100 %, and results in a lower CH_4 conversion and a lower CH_4 conversion ratio.

To further verify that the degree of MnO_x promotion is indeed dependent on the availability of the gas phase O_2 , the same experiment was performed at a fixed space velocity and at varying temperatures (see Fig. 6(b)). As the gas-phase O_2 conversion increases with temperature, the promotional effect of MnO_x also increases.

The effect of MnO_x promotion on CH_4 activity was also investigated as a function of reaction temperature (see Fig. 6(a) and (c)). A simple comparison reveals that the effect of MnO_x promotion is even higher at a lower reaction temperature. For example, at similar O_2 conversions (*e.g.*, $\sim 30\%$) for the supported $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst, the conversion ratio at 800°C (~ 1.21) is lower than that at 750°C (~ 1.36).

The effect of the CH₄/O₂ ratio on MnO_x promotion was next examined (see Fig. 6(d)). The gas phase O₂ conversion only slightly decreases for the range of CH₄/O₂ ratios. The availability of gas phase oxygen, however, decreases significantly with increasing CH₄/O₂ ratio due to the inherent nature of the experimental conditions imposed. Thus, the MnO_x promotion effect increases with increasing CH₄/O₂ ratio.

The effect of MnO_x on OCM reaction product selectivity was also investigated as a function of reaction temperature and presented in Fig. 7. For the supported 5Na₂WO₄/SiO₂ catalyst, only small variations in the C₂, CO₂ and CO selectivity values were observed with changing reaction temperature while the CH₄ conversions increased. For the supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst, however, the C₂ and CO selectivity values show a noticeable increase and CO₂ selectivity drastically diminishes with increasing reaction temperature.

4. Discussion

4.1. Dynamics of supported Mn-Na₂WO₄/SiO₂ catalyst structure

Structure of supported Mn-Na₂WO₄/SiO₂ catalyst in oxidizing environments: The freshly calcined, dehydrated 1.2Mn-5Na₂WO₄/SiO₂ catalyst possesses crystalline Mn₂O₃, Na₂WO₄ and β -cristobalite (SiO₂) phases at 400 °C in an oxidizing environment (see Fig. 2 and Fig. 3). Surface Na-WO_x and MnO_x sites are also present on the SiO₂ support (see Fig. 3). The supported crystalline Na₂WO₄ phase is not present at 900 °C (see Fig. 2 and Fig. 3) due to melting above 700 °C. [7], [8], [9], [10], [11], [12], [13], [15], [16], [17] In contrast, the crystalline Mn₂O₃ phase, and surface Na-WO_x and MnO_x sites are stable at 900 °C in an oxidizing environment.

Structure of supported Mn-Na₂WO₄/SiO₂ catalyst in OCM reaction environments: Under OCM reaction conditions (900 °C), only the molten Na₂WO₄ phase and surface Na-WO_x and MnO_x sites are present on the β -cristobalite (SiO₂) support (see Fig. 3). The crystalline Mn₂O₃ phase, however, is absent under OCM (see Fig. 3). A previous *in-situ* Raman investigation on the bulk Mn₂O₃ phase showed that at high temperature (> 500 °C) and under inert (only He flow) or reducing (CH₄:O₂ 1:6) environment, the Mn₂O₃ phase transforms to the Mn₃O₄ phase upon reduction. [40] In the present study under OCM reaction at 900 °C, however, the Raman band for the crystalline Mn₃O₄ phase (~650 cm⁻¹) was not detected (see Fig. 3). [44] The absence of the crystalline Mn₃O₄ phase could be due to thermal broadening at high OCM reaction temperature or simply because the crystalline Mn₃O₄ phase does not exist owing to a net reducing gas environment (CH₄:O₂:N₂ 3.3:1:4). The absence of crystalline Mn-oxide phase during OCM reaction is also in agreement with previous *in-situ* XRD studies. [11] (The NAP-XPS data (see Fig. S1) show that Mn is present as both Mn³⁺ and Mn²⁺ oxidation states in the OCM environment. However, the 600 °C temperature for the NAP-XPS measurement is below that required for the OCM reaction.) Upon cooling to lower temperatures (400 °C and 120 °C), the crystalline Mn₂O₃ and Na₂WO₄ phases reappear. The crystalline Mn₂O₃ phase reappears because CH₄ is not able to reduce the Mn₂O₃ phase at these lower temperatures, but Mn₃O₄, if present, can be oxidized by gas-phase molecular O₂. The crystalline Na₂WO₄ phase reappears because these temperatures are below its melting point (~700 °C).

Differing conclusions can be found in the literature regarding the nature of manganese oxide phases in different gas environments and temperatures. In agreement with our findings, a few studies report the presence of the Mn_2O_3 phase under oxidizing environments and OCM relevant temperatures. [7], [16] In contrast, other studies observed the Mn_2O_3 phase in oxidizing environments and only low temperatures. [9], [10] At high temperatures and oxidizing environments, the Mn_2O_3 phase was seen to transform to the crystalline MnWO_4 phase during melting of Na_2WO_4 . [9] Alternatively, the presence of large amounts of $\text{Mn}_7\text{SiO}_{12}$ (with trace amount of MnWO_4) is also reported to be present under oxidizing environments and OCM relevant temperature. [11], [13] The current studies, however, did not detect the presence of crystalline $\text{Mn}_7\text{SiO}_{12}$ or formation of the crystalline MnWO_4 phase in the oxidized supported 1.2Mn-5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst (see Fig. 2 and Fig. 3). Under the OCM reaction environment, a few *in-situ/operando* XRD studies reported the disappearance of the crystalline Mn_2O_3 phase, which is in agreement with the current findings (see Fig. 3). The formation of crystalline Mn_2O_3 or $\text{Mn}_7\text{SiO}_{12}$ phases were also detected during an inert or OCM reaction gas environment. [11], [13] A possible reason for the formation of the crystalline $\text{Mn}_7\text{SiO}_{12}$ phase may be related to the type of starting SiO_2 support used by different researchers. [48].

In summary, the current findings reveal that the oxide phases present for the supported 1.2Mn-5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst under OCM reaction conditions are the molten Na_2WO_4 phase and the surface Na- WO_x and MnO_x sites on the crystalline β -cristobalite (SiO_2) support.

4.2. Formation of new surface Na- WO_x sites on SiO_2 during OCM

Heating supported 1.2Mn-5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts above the melting point of crystalline Na_2WO_4 ($\sim 700^\circ\text{C}$) also results in the formation of isolated surface Na- WO_x sites (Raman bands at 950 and 330 cm^{-1} , see Fig. 3). Consequently, both isolated surface Na- WO_x sites and the molten Na_2WO_4 phase (broad bands at 926, 808 and 305 cm^{-1}) co-exist under OCM reaction conditions. Interestingly, the intensity of Raman vibrations from surface Na- WO_x sites (946 and 330 cm^{-1}) has increased considerably after treatment under OCM reaction conditions (see Fig. 3). Such relative increase in the intensity of surface Na- WO_x species was also observed for the 5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst. [15] Additionally, the O1s lines from the NAP-XPS experiments show that the relative intensity of the oxygen peak from active metal oxide phases considerably increases in comparison to the oxygen associated with the SiO_2 support (see Fig. S1 and associated discussion) after catalyst treatment under OCM reaction conditions. All the above observations and discussion suggest that new surface WO_x sites are formed during OCM reaction.

4.3. Interaction between active metal oxide phases during OCM

Additional data processing was undertaken to examine the Raman shifts of the Na_2WO_4 phase (from 926 to 923 cm^{-1}) and surface Na- WO_x sites (from 950 cm^{-1} to 946 cm^{-1}) of the supported 1.2Mn-5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst after exposure to the OCM reaction environment (see Fig. 3, Fig. S4 and associated discussion). The comparative analysis between the supported 5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ and 1.2Mn-5 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts suggest the interaction of Mn with both the molten Na_2WO_4 phase and surface Na- WO_x sites during OCM. The interaction of Mn with molten Na_2WO_4 phase has previously been reported with *in-situ* Raman spectroscopy, in agreement with the current findings. [16] Furthermore, an *in-situ* Raman spectroscopic comparison of the

supported $5\text{WO}_x/\text{SiO}_2$ and $0.7\text{Mn}-3\text{WO}_x/\text{SiO}_2$ catalysts was undertaken to examine the possible interaction of MnO_x with surface WO_x sites (see Fig. S5 and associated discussion). The Raman spectra of the dehydrated catalysts showed the presence of surface $\text{Mn}-\text{WO}_x$ sites (~ 924 and 944 cm^{-1} , perturbed from 984 and 1014 cm^{-1} bands for the supported WO_x/SiO_2 catalyst with additional presence of crystalline MnWO_4 phase). This confirms that MnO_x can interact with

surface WO_x sites on SiO_2 and is reflected in perturbation of the $\text{W}-\text{O}$ vibration of the surface WO_4 sites. To the best of our knowledge, the interaction between surface MnO_x species and W-oxides (molten Na_2WO_4 phase and surface $\text{Na}-\text{WO}_x$ sites) on SiO_2 for supported $\text{Mn}-\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts during the OCM reaction has been shown, for the first time, *via* direct spectroscopic experiments.

The interaction of Mn with both the surface $\text{Na}-\text{WO}_x$ sites and molten Na_2WO_4 phase is also apparent from the H_2 -TPR experiments (see Fig. S3 and Fig. 4). The freshly calcined supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ and $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts exhibit similar TPR profiles. However, only the supported $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst was able to maintain a constant peak reduction temperature and total number of reducible O-atoms after several cycles of oxidation reductions. Moreover, even for the fresh catalysts, the number of removable O-atoms (associated with both surface $\text{Na}-\text{WO}_x$ species and Na_2WO_4 phase) from $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst is more than 10 % higher than the $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst. The above observations strongly support an interaction between Mn and W-oxide (surface $\text{Na}-\text{WO}_x$ species as well as Na_2WO_4 phase) and is consistent with previous literature findings [16], [35].

4.4. Active site(s) in supported $\text{Mn}-\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst for catalytic OCM reaction

Although the supported $1.2\text{Mn}/\text{SiO}_2$ catalyst is capable of activating CH_4 , its C_2 selectivity is significantly lower than that of the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts (with or without Mn promotion). The addition of MnO_x to the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst, however, significantly improves the CH_4 reactivity without affecting the C_2 selectivity (see Table 1). This suggests, in contrast to many proposals in the literature [7], [24], [25], [26], [27], [28], that the Mn-oxide by itself cannot be the selective active center for the OCM reaction to form C_2 product, but serves as a promoter for the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts to improve catalytic OCM activity without compromising C_2 selectivity. This observation also suggests that the W-oxide (surface $\text{Na}-\text{WO}_x$ sites and molten Na_2WO_4 phase) phases are the active sites for the catalytic OCM reaction [3], [19], [20], [21], [22], [23], [49].

4.5. Contribution of MnO_x towards catalytic OCM reaction network

Deeper insights into the role of MnO_x in the catalytic OCM reaction network were gained from TAP experiments (see Fig. 5). The O_2 - $^{13}\text{CH}_4$ pump-probe experiment revealed that the promotion with MnO_x significantly increases the total number of labile O_2 released from the surface (associated with molten Na_2WO_4 phase) from the $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst. [35] The production of C_2H_6 , however, was minimally affected suggesting the surface $\text{Na}-\text{WO}_x$ sites are mostly responsible for the formation of the C_2H_6 product. In contrast, the CO_2 yield was significantly enhanced, relating its origin to the molten Na_2WO_4 phase. The involvement of W-oxide phases

towards CH₄ activation in the OCM reaction is in agreement with many previous findings [3], [16], [19], [20], [21], [22], [23].

Further, the O₂-C₂H₆ pump-probe experiment showed significant improvement in C₂H₄ production in the presence of Mn (and concomitant higher amount of released O₂ from the molten Na₂WO₄ phase), suggesting that the molten Na₂WO₄ phase is also responsible for oxidative dehydrogenation of C₂H₆ to C₂H₄. [15] This result is also confirmed by the steady state OCM reaction studies (see Table 1). [15], [50] The reactivity data and product distribution suggest that (i) Mn-oxide is only modestly effective as a dehydrogenation center for C₂H₆ to C₂H₄ oxidative conversion since its dehydrogenation capability is even lower than the supported 5Na₂WO₄/SiO₂ catalyst, (ii) the addition of MnO_x to the supported 5Na₂WO₄/SiO₂ catalyst, however, improves the C₂H₄ product selectivity that is related to a greater number of dioxygen species available from the molten Na₂WO₄ phase.

4.6. Influence of gas-phase molecular O₂ concentration on MnO_x promotion

The catalytic OCM reaction over the supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst has been proposed to follow a hybrid Mars-van Krevelen redox type mechanism by many studies. [3], [13], [17], [30], [31], [32], [33], [34], [37] This suggests that the oxygen species from the active oxide phases becomes consumed in the oxidation reaction steps and then gets replenished by the gas phase oxygen. Thus, the OCM activity is expected to depend on both the gas phase O₂ concentration and the exchange rate of oxygen between the gas phase and catalyst lattice. From catalytic OCM activity data in Fig. 6, one can clearly see that the MnO_x promotion strongly depends on gas phase O₂ concentration. When sufficient gas phase molecular O₂ is present, the MnO_x promotion effect is low. In contrast, the MnO_x promotion gradually becomes significant with a decrease in gas phase molecular O₂ concentration (or higher O₂ conversion), suggesting that the MnO_x sites play a mediator role for oxygen exchange between the gas phase and catalyst lattice. To further elaborate on this, the oxygen exchange happens in both ways: (i) the gas phase O₂ is supplied to the reduced catalytic oxide phase by the MnO_x center. This is evident by the cyclic H₂-TPR experiment (see Fig. 4) where the supported 5Na₂WO₄/SiO₂ catalyst regains almost all lattice oxygen species during the reoxidation step only in the presence of MnO_x species. (ii) Catalytic oxygen is supplied to the catalyst surface for consumption. Thus, the presence of MnO_x species increases the total amount of oxygen release that results in significant improvement in catalytic performance (activity as well as selectivity) [15], [35].

The current conclusions are in agreement with many literature reports claiming that MnO_x participates in oxygen spillover to the W-oxide centers. [3], [17], [19], [20], [21], [22], [23] Recent *in-situ/operando* XRD and Raman studies reported that the oxygen exchange between gas phase and catalyst oxide lattice takes place *via* the reversible cycle of Mn₇SiO₁₂ ↔ MnWO₄. [13] Other *ex-situ* studies speculated the Mn₂O₃ ↔ MnWO₄ redox cycle to be operational for oxygen exchange. [51], [52] Such 3D oxide phases, however, were not detected in the current study with the supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst during OCM. It is, thus, proposed that the thermally and chemically stable surface MnO_x sites in the current 1.2Mn-5Na₂WO₄/SiO₂ catalyst are responsible for facilitating oxygen exchange between gas-phase molecular O₂ and the W-oxide phases.

4.7. Influence of temperature on MnO_x promotion

At similar oxygen conversion, the promotional effect of MnO_x on CH₄ activity was found to be higher at lower reaction temperatures (see Fig. 6(a) and (c)). This observation is in agreement with literature reports that observed MnO_x promotion allows the catalyst to conduct the OCM reaction at a much lower reaction temperature than for the unpromoted, supported 5Na₂WO₄/SiO₂ catalyst. [29] However, the CH₄ can be activated by both the surface Na-WO_x sites and molten Na₂WO₄ phase. [15] For the supported 5Na₂WO₄/SiO₂ catalyst, the C₂ and CO (primarily formed by surface Na-WO_x species), and CO₂ (mostly coming from the molten Na₂WO₄ phase) [15] selectivity values do not change significantly with increasing reaction temperature (see Fig. 7). This suggests the activity of both of these sites increase proportionately with temperature, in the absence of MnO_x species. In contrast, for the supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst, the C₂ and CO selectivity increase, and CO₂ selectivity decreases with temperature. Such an interesting change in the selectivity of C₂ and CO (increasing with temperature) and CO₂ (decreasing with temperature) is also reported in the OCM literature for 1.2Mn-5Na₂WO₄/SiO₂ catalyst, both at atmospheric and elevated pressures (0.2–0.4 MPa). [46], [53] These observations suggest that MnO_x selectively promotes the molten Na₂WO₄ phase at lower temperature and that the MnO_x promotion of surface Na-WO_x sites becomes dominant at higher temperatures.

5. Conclusions

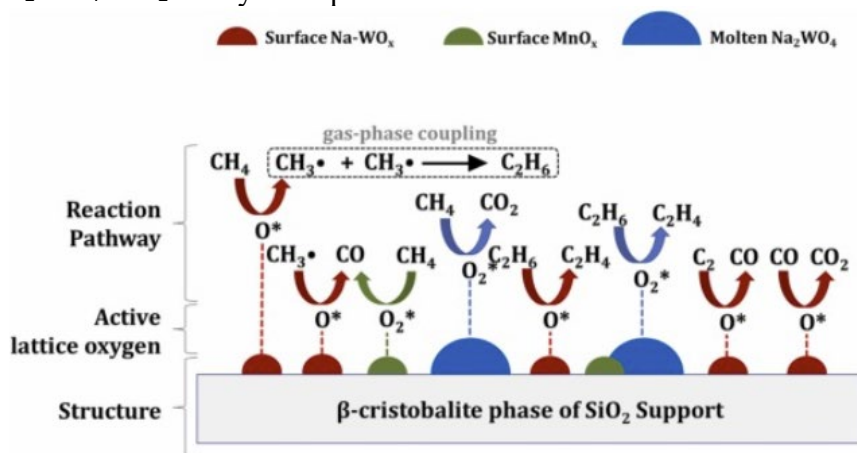
The structural dynamics of the supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst under OCM reaction conditions were investigated with multiple *in-situ* characterization techniques and chemical probe measurements. The role and promotional effect of MnO_x phase was investigated *via* controlled TAP experiments and detailed steady state kinetic studies. The findings are summarized as follows:

- (i)
The freshly calcined, dehydrated 1.2Mn-5Na₂WO₄/SiO₂ catalyst contains (at 400 °C, oxidizing environment) crystalline Mn₂O₃, Na₂WO₄ and β-cristobalite (SiO₂) phases along with surface MnO_x and Na-WO_x sites. Heating the catalyst to 900 °C (oxidizing environment) results in melting of the crystalline Na₂WO₄ phase. Interestingly, the WO₄ structure originally present in Na₂WO₄ crystal is preserved in its molten phase.
- (ii)
In the OCM reaction environment at 900 °C, the Mn₂O₃ crystalline phase disappears, possibly due to the reduction of Mn-oxide. In contrast, the surface MnO_x and Na-WO_x sites exhibit excellent thermal and chemical stability and Na₂WO₄ remains in molten phase.
- (iii)
Deeper analysis of the *in-situ* Raman spectra provided the first ever direct spectroscopic evidence regarding the interaction between Mn and W-oxide (molten Na₂WO₄ phase and surface Na-WO_x sites) centers. Further analysis revealed that the treatment of the supported 1.2Mn-5Na₂WO₄/SiO₂ catalyst in the OCM reaction environment results in formation of new surface Na-WO_x sites from redispersion of molten Na₂WO₄ phase on the SiO₂ support [15].
- (iv)

The MnO_x species are active towards CH_4 conversion, but not selective. The addition of MnO_x to the supported $5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts, however, significantly improves the catalyst activity without affecting the C_2 selectivity. This suggests that the W-oxide centers are the catalytic active site for OCM and that the MnO_x species *only* act as promoters in the supported $1.2\text{Mn}-5\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst.

- (v)
The promotional effect of MnO_x is strongly dependent on the reaction conditions. At low availability of gas-phase molecular O_2 , the promotional effect becomes significant suggesting MnO_x species act as mediators for oxygen exchange between the gas phase and catalyst lattice.
- (vi)
 MnO_x promotion of the catalytically active molten Na_2WO_4 phase and surface $\text{Na}-\text{WO}_x$ sites varies as a function of reaction temperature. At low temperature, the MnO_x species selectively promote the molten Na_2WO_4 phase and at high temperature the MnO_x promotion of the surface $\text{Na}-\text{WO}_x$ sites becomes dominant.

These new findings add clarity to the debates in the literature regarding stable structures, role, and promotional effect of MnO_x in the supported $\text{Mn}-\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst during the OCM reaction. Based on the new findings from this study, along with the findings from the published articles [15], [35], we propose the OCM reaction mechanism to take place over supported $\text{Mn}-\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts as presented in Scheme 1.



Scheme 1. OCM reaction mechanism over supported $\text{Mn}-\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts.

CRedit authorship contribution statement

Sagar Sourav: Conceptualization, Methodology, Validation, Investigation, Writing – original draft. **Daniyal Kiani:** Conceptualization, Methodology, Writing – review & editing. **Yixiao Wang:** Conceptualization, Methodology, Validation, Writing – review & editing, Supervision. **Jonas Baltrusaitis:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition. **Rebecca R. Fushimi:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition. **Israel E. Wachs:** Conceptualization, Methodology, Writing – review & editing, Supervision, 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.

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