Low-Temperature Catalytic Methane Deep Oxidation over Sol-gel derived Mesoporous Hausmannite (Mn$_3$O$_4$) Spherical Particles

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Abstract

Herein, Mn$_3$O$_4$ spherical particles (SPs) were synthesized by the sol-gel process, followed by thermal annealing at 400 °C. The sample was analyzed by XRD, FTIR, SEM, $S_{\text{BET}}$, XPS, H$_2$-TPR and UV-vis spectroscopy. XRD and FTIR analysis show that Mn$_3$O$_4$ exhibits a tetragonal spinel structure. SEM and $S_{\text{BET}}$ analysis display a porous homogeneous surface made of strongly agglomerated spherical-like grains size with an estimated average particle size of ~35 nm, corresponding to a large specific surface area ($S_{\text{BET}}$) of ~81.5 m$^2$/g. XPS analysis indicated that, Mn$_3$O$_4$ were composed of metallic cations (Mn$^{4+}$, Mn$^{3+}$, Mn$^{2+}$) and oxygen species (O$^{2-}$, OH$^-$ and CO$_3^{2-}$). The optical energy band gap energy was ~2.55eV. Moreover, Mn$_3$O$_4$ SPs were successfully tested as catalyst with almost 100% conversion of CH$_4$ to CO$_2$ and H$_2$O at a gas hourly space velocity (GHSV) of 72 000 mL$^3$.g$^{-1}$h$^{-1}$. The observed performance can be assigned to the cooperated effects of the smallest spherical-like grain size with mesoporous structure as responsible for the larger $S_{\text{BET}}$, and the available surface-active oxygenated species. The cooperative effect of the good reducibility, the higher ratio of active species (O$_{\text{Lat}}$/O$_{\text{Ads}}$), as well as Density Functional Theory (DFT) calculations suggested that, CH$_4$ total oxidation over the mesoporous Mn$_3$O$_4$ SPs might follow a two-term process in which both Langmuir-Hinshelwood and Mars-van Krevelen mechanisms are cooperatively involved.

**Keywords:** Sol-gel; Manganese oxide; Catalytic oxidation; Methane; Langmuir-Hinshelwood mechanism; Mars-van Krevelen route; Two-Term process.
1. Introduction

Methane (CH$_4$) is a strong greenhouse gas exhibiting a global warming capacity exceeding thirty times that of carbon dioxide (CO$_2$). [1] CH$_4$ is extensively employed in numerous applications including heating and power generator systems. Today, the dismiss of unburnt CH$_4$ into the atmospheric air mainly from transport and industrial activities using natural gas is responsible of severe environmental issues. [2] Therefore, it is increasingly urgent to decrease the emission of CH$_4$ into the environment and catalytic combustion stands as prominent applied remediation technic to convert CH$_4$ into CO$_2$ and H$_2$O known as a less harmful species. To date, total oxidation of CH$_4$ by heterogeneous catalysis not only enables the drastic reduction of reaction temperatures but also limits SO$_x$, NO$_x$ and CO emissions. [3,4] For this purpose, distinct variety of catalysts such as precious metals and transition metals oxides (TMOs) are largely applied for catalytic oxidation. Supported precious metals ccatalysts including Au, Pt, Pd, Rh and Ir have demonstrated excellent performances in CH$_4$ oxidation reactions. [5-7] As an example, Pd supported catalyst in particular has demonstrated outstanding activity in the CH$_4$ total oxidation at low above 400°C. [8-10] However, this type of catalyst presents major drawbacks such as the availability, poisoning tendency as well as sintering at high temperatures that leads to a loss of their performance. [11,12] In contrast, TMOs although slightly less active than precious metals catalysts, are available and less expensive, more resistant to poisoning (chlorine, sulfur, etc.), exhibits high thermal stability, variable oxidation states. [13,14] In addition, the physicochemical properties as well as the catalytic activity can be tuned using synthesis doping strategy. [15,16,17] Among various TMOs applied for the CH$_4$ catalytic oxidation, Mn oxides such as $\alpha$-MnO$_x$, $\alpha$-Mn$_2$O$_3$, $\gamma$-MnOOH, and Mn$_3$O$_4$ have received much attention thanks to their specific physicochemical properties. [18,19] In the group of Mn oxide catalyst, $\alpha$-MnO$_2$ is a promising alternative to noble metals and is intensively applied for the CH$_4$ total conversion to H$_2$O and CO$_2$. An extensive illustration of the mechanism involved in CH$_4$ total oxidation studied by Wang et al. and Hu et al., suggested that CH$_4$ total oxidation over MnO$_2$ may follow the Langmuir-Hinshelwood Mechanism (L-H) with an indirect Mars-van Krevelen (MvK)
route that involves lattice, [19] hanging on the of oxygen vacancies (O\textsubscript{vac}) formation. However, the catalytic performance of MnO\textsubscript{2} is still not efficient at low temperatures. CH\textsubscript{4} has much tighter C-H bonds (450 KJ/mol) in its molecule that are difficult to break and therefore require high temperatures. [20] Thus, the challenge remains to design a material that is stable at high temperatures and can be active over a long period of operation. Previous investigation by Tian et al. reports the lattice thermal stability limit of Mn\textsubscript{3}O\textsubscript{4} to be up to 800 °C with an excellent performance towards propene oxidation between 350 and 500 °C. Mn\textsubscript{3}O\textsubscript{4} is, therefore, an appropriate catalyst suitable for high-temperature oxidation processes such as CH\textsubscript{4} total conversion.

In general, Mn-oxides structure and the population of Mn (III) at the surface play a decisive role in their catalytic reactivity. [21] The catalytic performance of Mn-oxides is strongly dependent on the catalyst’s atomic configuration, crystallographic structures, morphology and pore structures. Mn\textsubscript{3}O\textsubscript{4} has a structure of tetragonally distorted spinel (to the Jahn–Teller effect on Mn\textsuperscript{3+} ions) with Mn (II) occupying the tetrahedral (Tet) sites and the Mn (III) locating the octahedral (Oct) sites of the normal spinel structure. [22] Mn\textsubscript{3}O\textsubscript{4} presents diverse polymorphic structures with variable means to connect together with the basic Oct units that can display outstanding different catalytic performance. [18] Despite the above-mentioned properties favourable for their application as a catalyst, Mn\textsubscript{3}O\textsubscript{4} is more often used as a noble metal catalyst carrier in CH\textsubscript{4} oxidation reactions rather than an active phase like MnO\textsubscript{2}. [23] Moreover, a systematic study on the CH\textsubscript{4} oxidation over Mn\textsubscript{3}O\textsubscript{4} has not been yet established.

In the present study, Mn\textsubscript{3}O\textsubscript{4} SPs catalysts were prepared by sol-gel technic, and their physicochemical properties including XRD, FTIR, SEM, EDX, S\textsubscript{BET}, and XPS were systematically and comprehensively characterized. The temperature-programmed reductions under dihydrogen flow (H\textsubscript{2}-TPR), as well as UV-visible spectroscopy were investigated to assess reduction property and quantify the optical energy band gap (E\textsubscript{g}\textsuperscript{opt}) of Mn\textsubscript{3}O\textsubscript{4} NSs. Moreover, the performance and stability towards the total conversion of CH\textsubscript{4} were evaluated. In addition, in-situ DRIFTS approach was employed to study the most prominent reaction mechanism involved in the CH\textsubscript{4} oxidation onto
the Mn₃O₄ surface. The catalytic performance of the Mn₃O₄ SPs catalyst was correlated to their tailored physico-chemical characteristics. More importantly, Density Functional Theory (DFT) calculations were carry out to monitor both adsorption and dissociation of CH₄ molecule at the Mn₃O₄ (001) catalysts surface and identify the reaction pathway involved in the CH₄ oxidation on the surface of mesoporous Mn₃O₄ SPs catalysts.

2. Results

2.1. The crystal structures

XRD and FTIR analysis of the sol-gel derived Mn₃O₄ SPs was performed, and the diffractograms are presented in Figure 1. Figure 1a presents the XRD spectrum of Mn₃O₄. As it can be appreciated from Fig. 1a, the hkl reflections at (112), (200), (103), (121), (004), (220), (105), (303), (321) and (224) corresponding to 2θ values of 29.07, 30.97, 32.6, 35.89, 38.75, 44.1, 51.9, 56.1, 58.15, 60.1, and 64.03° match well with the characteristic diffraction patterns of Mn₃O₄. The overall diffraction peaks of the as-prepared Mn₃O₄ SPs, annealed at 400 °C matched well with standard reference patterns ((JCPDS card no. 24-0734) characteristic of Mn₃O₄ with hausmannite structure (space group I41/amd). [24,25] From the XRD spectrum, no peaks characteristics of impurities were detected, attesting of the purity of the sample. The standard grains size estimated from the XRD was ~17 nm.

The FT-IR spectrum was also recorded (400-4000 cm⁻¹) as displayed in Fig. 1b, in order to supply qualitative details on the functional groups present at the surface of Mn₃O₄ SPs. From the Mn₃O₄ spectrum, five prominent peaks were observed. The peaks located at 3441 and 1693 cm⁻¹ is assigned to the stretching vibration mode of OH (form H₂O) and the bending mode of H₂O molecules respectively. Moreover, the vibration frequency located at ν₁ = 654 cm⁻¹ correspond to the intrinsic stretching vibration of the metal ion at the tetrahedral site (υM₄t-O), while the bands at ν₂ = 556 cm⁻¹ correspond to the distortion vibration of Mn-O in an octahedral environment.

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Finally, the third vibration signal located at 462 cm\(^{-1}\) is assigned to the Mn species (Mn (III)) vibration in the octahedral site of Mn\(_3\)O\(_4\). [26,27]

**Figure 1**

### 2.2. Surface morphology and EDS elements mapping

Figure 2 (a, b, and c) shows the low and higher magnification SEM micrographs as well as the particles size distribution of Mn\(_3\)O\(_4\) respectively. Figure 2a exhibits a low magnification SEM micrograph of Mn\(_3\)O\(_4\) displaying a homogeneous surface, covered with large amounts of interconnected small spherical-like grains size with apparent porosity. The high magnification SEM image of the Mn\(_3\)O\(_4\) sample reveals the increase of these grains resulting from their agglomeration and the emergence of huge particles with a spherical-type structure. As shown in Fig.2b, particle sizes are in the range of 20 to 50 nm with an average size of ~35 nm (Fig 2c) are randomly distributed at the Mn\(_3\)O\(_4\) surface. To confirm the existence of each element, an element mapping analysis was performed. The mapping was obtained from the SEM image as displayed in Fig. 2(d, e), and the distribution of each component at the surface of the Mn\(_3\)O\(_4\) NSs was in close agreement with earlier study. [28] The high density of red dots in Fig. 2d constitutes the densely dispersed Mn atoms while the green color account for the presence of oxygen atoms in Mn\(_3\)O\(_4\) SPs (Fig. 2e). Such a surface morphology with a porous-like structure generally provides a more exposed surface contact for the reactant molecules that will be favorable for the catalytic activity. [15,16]

**Figure 2**

### 2.3. Porosity and BET-specific surface areas (S\(_{BET}\)) analysis

Fig. 3 displays the N\(_2\) adsorption/desorption isotherms (BET) and the pore size distributions (BJH) of Mn\(_3\)O\(_4\) nanospheres. As shown in Fig 3a, the shape of the N\(_2\) absorption/desorption isotherm at the surface of Mn\(_3\)O\(_4\) SPs is seemingly similar to type IV with H\(_3\)-type hysteresis loops. [29] According to IUPAC, materials with such feature is generally classified as mesoporous. The S\(_{BET}\) and pore size (PS) of the NSs were estimated to be ~81.5 m\(^2\)/g, and ~30 nm, respectively. Mn\(_3\)O\(_4\) SPs with mesoporous configuration and the substantial PV is awaited to provide more
available and active sites, which will be beneficial for the enhancement of catalytic process. The expected enhancement of the catalytic reaction will be discussed with respect to the adsorption and diffusion promotion, and the decline of the interphase mass transfer. [30]

**Figure 3**

2.4. Elemental chemical configuration and oxidation states analysis

The elemental chemical configuration displaying Mn and O atoms oxidation state of the Mn₃O₄ SPs was analysed using X-ray photoelectron spectroscopy (XPS). XPS spectra depicted on figure 4 confirms the presence of Mn and O elements and no other elements or impurities were detected in agreement with XRD and FTIR analysis. High-resolution XPS spectra presented in Fig. 4a, display the characteristic peaks of the Mn 2p, obtained in the binding Energy (BE) between 638 and 657 eV. Because of the occurrence of spin-orbit splitting, the Mn 2p signal is resulted to two mains signals: Mn 2p₃/2 and Mn 2p₁/2 located at 641.37 and 652.87 eV respectively with BE difference of 11.5 eV in excellent accordance with the literature. [18, 31] In the interest of determining the possible Mn oxidation states, both Mn 2p₃/2 and signals Mn 2p₁/2 were deconvoluted by applying the Gaussian–Lorentzian function. This indicates the existence of Mn atoms with three oxidation states (Mn(II) Mn(III), and Mn(IV) in the Mn 2p₃/2 peak with BE located 640.82, 642.14, and 643.12 eV respectively, whereas the corresponding signals in the Mn 2p₁/2 peak is detected at 652.53, 653.61 and 654.54 eV. The BE values characteristic of Mn atoms in Mn₃O₄ SPs in the present work are in good accordance with the earlier results in the literature. [31-33] Hausmannite (Mn₃O₄) in this study presents characteristics of a normal spinel structure in which different oxidation Mn are regularly distributed in the Tet sites (Mn²⁺) and Oct sites (Mn³⁺) as follow [Mn²⁺]₅₆[Mn³⁺, Mn³⁺]₀₄ O₄.

To further assess the existence of oxygenated species at the surface of Mn₃O₄ SPs and confirm the variation in the oxidation states of Mn in the course of the redox process, XPS O 1s core-shell was analysed and present in Figure 4(b). From the Fig. 4(b), O 1s XPS spectra exhibits
two strong signals centered at the BE of 529 and 531±0.2 eV. Both signals were resolved into three constituents: the signal located at 529.73±0.2 eV is assigned to the Mn–O–Mn surface oxygenated species (O−, O2−, O2−) also known as Lattice oxygens (O_{Lat.}) in the vicinity of the surface vacancies [34]. The peak centered at 531.28±0.2 and 532.68±0.2 eV are ascribed to the adsorbed oxygen (O_{Ads.}) species such as hydroxyl and (OH−) and carbonyl group (CO32−), adsorbed on Mn3O4 surface in close agreement with earlier reported studies. [34, 35] The variation in the relative intensity of the overall surface oxygenated species (Mn–O–Mn and OH and CO32−) is due to the change in the oxidation state of Mn atoms. The detected active oxygenated species including surface oxygen species and highly reactive O_{Lat.} are generally easily involved catalytic oxidation process.

**Figure 4**

2.5. Temperature-programmed reduction under H2 flow analysis (H2-TPR)

The H2-TPR was investigated in the temperature ranging from 50 to 600 °C, to study the reducibility of Mn3O4 SPs and the result is presented in Fig. 5. The recorded spectrum exhibits two prominent reduction signals centered at ≈ 268 and ≈ 430 °C respectively. Each signal was resolved into three distinct reduction peaks centered at (200, 268 and 310 °C) and (375, 430 and 470 °C) which can describe the reduction of Mn3O4 as follows: MnO2 → Mn3O4 → MnO. [36] Generally, the reduction peaks in the temperature range of 210 to 298 °C can be assigned to the of MnO2 → Mn3O4 or eventually Mn2O3 → Mn3O4 whereas, those in the temperature range of 403 to 460 °C can be ascribed to the reduction of Mn3O4 → MnO in agreement with the literature. [36,37] It is worth mentioning that, the signals ranging from 210 to 298 °C correspond either to the surface oxygen species and highly reactive O_{Lat.}[34] or to the occurrence of narrow particles size on Mn3O4 NSs. The XPS and H2-TPR results are in agreement and suggest that, Mn3O4 catalytic performance could be significantly and remarkably enhanced by the actives species (Mn2+/Mn3+/Mn4+, O−, O2−, O2−) and good reducibility capacity. [36,37]

**Figure 5**
2.6. Optical energy band gap study ($E_g^{\text{Opt}}$)

UV-Vis absorption spectrophotometer was used to record characteristic spectrum of Mn$_3$O$_4$ SPs and estimated throughout Tauc equation $E_g^{\text{Opt}}$. Typical spectrum is displayed in figure 6 and clearly identify the characteristic absorption bands decreasing as the wavelength towards the visible region increase, in line with the literature data. [38,39] The optical bandgap energy was estimated from the obtained absorption spectra using the Tauc law:

$$\alpha h\nu = (h\nu - E_g)^{1/2}$$  \hspace{1cm} (1)

where ($\alpha$) represents the absorption coefficient and ($h\nu$) is the photon energy. The absorption spectrum was employed to evaluate the $E_g^{\text{Opt}}$ from $(\alpha h\nu)^2$ vs ($h\nu$) plot as presented in Fig. 6b. The estimated $E_g^{\text{Opt}} = 2.55$ eV is in accordance with the reported results. [38,39] A strong relationship between the $E_g^{\text{Opt}}$ and the performance of transition metal-based oxide catalysts was early established and reported in the literature. [17,40-42] Genuinely, catalysts made of TMOs with lower optical energy band gap substantially reveal excellent electron mobility which orderly enhances the mobility of oxygenated species (O$^-$, O$_2^-$, O$_2^{2-}$) in the vicinity of the surface void together with the reducibility, decisive in the catalyst successful advancement.

Figure 6

2.7. Catalytic behavior

2.7.1. Methane total oxidation performance and structure–activity correlations of the Mn$_3$O$_4$ SPs

The performance of the mesoporous Mn$_3$O$_4$ with agglomerated spherical-like structure morphology was investigated (Figure 7). The CH$_4$ exhaust profiles, and the spectra displaying the gas phase products formation as well as the stability/reproducibility test during the CH$_4$ oxidation process over Mn$_3$O$_4$ NS are displayed in Fig. 7a, b, and c respectively. The abatement of CH$_4$ was performed between 150 and 480 °C. From the Fig. 7a, it was observed that, the CH$_4$ conversion is obvious under 250 °C and progressively increases with the reaction temperature increase. CH$_4$ total oxidation over Mn$_3$O$_4$ reaches 10, 50, and 90 % conversion to CO$_2$ and H$_2$O at ~324, ~377 and 398 °C

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respectively. The IR spectra (Fig.3b) of gas phase outlet deriving from CH₄ conversion indicate that just 10% of CH₄ is converted at 324 °C. However, upon temperature increase, typical doublet peak characteristic of CO₂, in the wavenumber region raging from ~2205 to ~2460 cm⁻¹ increase progressively as the signals in the regions located at 3304 – 27620 cm⁻¹ and those 1225 – 1506 cm⁻¹ associated respectively with C-H stretching and C-H deforming vibrations of CH₄ molecule decrease. Finally, CH₄ totally disappear at T₁₀₀ = 403 °C attesting of the total oxidation of CH₄.

**Figure 7**

In addition, the reproducibility test, well established as an important criterium for catalysts intended for industrial application was carry out and presented in Figure. 7c. This test was performed to test Mn₃O₄ catalysts susceptibility to face thermal deactivation which is a limiting factor for their application in industrial scale. Mn₃O₄ SPs exhibits excellent CH₄ total oxidation in three consecutive repeated runs, testifying for its excellent stability and reproducibility. A comprehensive comparison with earlier reported TMOs in literature reveals that Mn₃O₄ exhibits outstanding performance in the catalytic combustion of CH₄, (see Table 1). As an example, the performance of several bulk TMOs (Co₃O₄, Mn₂O₃, Cr₂O₃, CuO, and NiO) catalysts in CH₄ total oxidation studied by Paredes et al., [43] reveals the following performance order: Co₃O₄ > Mn₂O₃ > Cr₂O₃ > CuO > NiO. Co₃O₄ was thus identified as the best candidate, owing to the unfilled 3d orbital of Co, the fragile strength of the Co–O bond, and the excellent redox cycle frequency as well as a low barrier of oxygen vacancy. Like Co₃O₄, Mn₃O₄ crystalize in a spinel structure and also exhibits a varied valence state of Mn (Mn²⁺, Mn³⁺, and Mn⁴⁺), and non-identical ways to connect to the basic octahedral units, thereby displaying remarkable and efficient catalytic activities for the CH₄ oxidation. [56, 57] Due to their similar chemical structure, oxidation degree, close standard reduction potentials [E⁰ (Co³⁺/Co²⁺) = 1.92; of, E⁰(Mn³⁺/Mn²⁺) = 1.54), CH₄ oxidation over Mn₃O₄ SPs could proceed following the same scheme. In fact, in the CH₄ catalytic oxidation process, activation is initiated and occurs on the Mn₃O₄ surface. The bounded O_ads. (OH and CO₃²⁻ group) on Mn₃O₄ will react easily with the surface adsorbed CH₄, resulting in more active site for CH₄ degradation. In addition, with the
existence of Mn$^{4+}$ known to be easily reducible at low temperatures, Mn$^{4+}$ cations are will reduced to Mn$^{3+}$ in the oxygen environment. It can thus be suggested that CH$_4$ can be activated by surface adsorbed oxygen species throughout the Langmuir-Hinshelwood (L-H) mechanism. The surface Mn$^{4+}$/Mn$^{3+}$ redox cycle can produce oxygen vacancies, promoting the both adsorption and activation of O$_2$ molecules that require O$_{\text{Lat.}}$ in the Mars-van-Krevelen (MvK) process. [58, 59] Hence, it is necessary to elucidate the reaction mechanism of CH$_4$ total conversion over mesoporous Mn$_3$O$_4$ SPs at a molecular scale.

**Table 1**

2.7.2. Possible reaction mechanism involved in CH$_4$ Oxidation

Divergent opinions on the probable mechanism involved in the CH$_4$ oxidation reaction over TMOs-based oxide have been reported in the literature, and are consistent with the mechanisms displayed in Figure 8. While some authors are favorable to the L-H mechanism involving the participation of surface adsorbed oxygen, others support Mvk process involving a strong contribution of the oxygen in the lattice. [60-64] Meanwhile, a two-term (T-T) mechanism that combines both L-H and MvK processes was also proposed. [62,65]

**Figure 8.**

**L–H mechanism** (Fig.8a): In this process, it is suggested that, in addition to the O$_{\text{Ads.}}$, generally present at the TMOs catalysts surface, gaseous O$_2$ with low adsorption activation energy compared to that of CH$_4$ is specially adsorbed onto the catalyst surface to generate supplementary O$_{\text{Ads.}}$. Therefore, the generated O$_{\text{Ads.}}$ will be easily combined with adsorbed CH$_4$, enabling the dissociation of hydrogen via electrophilic attack accompanied by the destruction of CH$_4$ stable structure and the production active methyl radicals (*CH$_3$–) as CH$_4$ oxidation promoters. It is worth to mention that, L-H process generally take part in low reaction temperature ranging from 250 to 400 $^\circ$C.

**MvK mechanism** (Fig.8b): Also known as intrafacial process, MvK is a redox process that involves surface oxygen reaction associated with O$_{\text{Lat.}}$ migration from the bulk to the TMOs catalysts.
surface. The mechanism consists of the surface adsorption and dissociation of CH$_4$ at the surface of the catalysts active sites to generate alkyl and hydroxyl groups, followed by spills over reaction in the presence of the O$_{\text{Lat.}}$ as the oxidizing agents and finally, generate CO$_2$ and H$_2$O. Subsequent to the desorption of reaction products, numerous lattice oxygen vacancies (O$_{\text{vac.}}$) are formed upon the reduction of active sites. The as-formed O$_{\text{vac.}}$ can be renewed by O$_{\text{Lat.}}$ propagation from the bulk position or by adsorption of gas phase O$_2$. MvK process is well established for a number TMOs including Fe$_2$O$_3$ and Co$_3$O$_4$. [60, 65, 66] The reaction temperatures generally above 375 °C facilitate the migration of the O$_{\text{vac.}}$ from the bulk to the catalyst surface.

**T-T process** (Fig.8c): In some situations, it is often challenging to describe the reaction pathway involved in the catalytic oxidation over TMOs by a single process. In that case, a cooperative process governed by both L–H and the MvK mechanism in which both surface O$_{\text{Ads.}}$ and O$_{\text{Lat.}}$ simultaneously take part in the reaction sequence is proposed. [65] Practically, molecular oxygen is simultaneously adsorbed and dissociates to form surface-active oxygen species, that will oxidize CH$_4$ simultaneously with surface O$_{\text{Lat.}}$ derived from the Bulk, and generating O$_{\text{vac.}}$. That will later be replenished by O$_2$ from the gas phase in excellent agreement with the literature. [67]

It has been well established that, the reaction mechanism in the catalytic oxidation over TMOs surface can differ based on catalyst physico-chemical properties and structure or on the catalytic test condition. In the present investigation, XRD, SEM and BET together with XPS and H$_2$-TPR analysis showed mesoporous Mn$_3$O$_4$ possessing nano-spherical particles, with higher surface specific area (81.5 m$^2$/g), good redox behavior (Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$) and adsorbed oxygenated species (CO$_3^{2-}$, OH$^-$). In addition, the reaction temperature plays a decisive task in the elucidation of the reaction mechanism. In the present study, it is observed from Fig. 7a that CH$_4$ oxidation take place in two reaction temperature domains: (a) in the low-temperature zone (250–375°C), CH$_4$ can be firstly stimulate by monatomic oxygen species at the surface of Mn$_3$O$_4$ SPs, where an easy decarboxylation and dihydroxylation occurs, leaving the catalyst surface in a stoichiometric stage, via L–H mechanism. Above 375°C, an intrafacial dihydroxylation and
decarboxylation of the catalyst stimulate the formation of the O\textsubscript{vacc.}, favoring a slight reduction of Mn\textsubscript{3}O\textsubscript{4} SPs surface. Then, the O\textsubscript{vacc.} are virtually renewed by O\textsubscript{2}, which attest of the coexistence of both L–H and MvK process.

From the systematic analysis of Mn\textsubscript{3}O\textsubscript{4} SPs and the obtained catalytic results, it is suggested that CH\textsubscript{4} can be initiated by active oxygen species adsorbed at the surface of Mn\textsubscript{3}O\textsubscript{4} SPs, via L-H mechanism. The L-H pathway may deal with an indirect oxidation scheme, involving O\textsubscript{L-at.} (MvK process) in close agreement with Han et al.;[65] who have studied the kinetics involved in the CH\textsubscript{4} combustion over α-Mn\textsubscript{2}O\textsubscript{3} catalysts and concluded that that the process involves T-T mechanism. Therefore, CH\textsubscript{4} oxidation over Mn\textsubscript{3}O\textsubscript{4} SPs in the present work may also proceed through a concerted T-T mechanism. To get more insight, Density Functional Theory (DFT) calculations were performed.

3.8 Density functional theory results

3.8.1. Computational details.

The Quantum-ESPRESSO package was utilized to perform DFT calculations. [68] The interactions between the ions core and valence electrons were treated using ultrasoft pseudopotentials. [69] The exchange and correlations effects were treated within the generalized gradient approximation (PBE). [70] To correctly describe the Mn 3d states, a Hubbard correction [71] of U=3.9 eV was considered. The structural optimization of atomic positions was performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm gradient method with force convergence threshold of 10−5 eV Å−1. A 4 × 34 × 4 k-point mesh was employed to sample the Brillouin zone of the bulk unit cells and the electronic wave functions were expanded using a plane wave cut-off energy of 40 Ry. A 16 Å × 16 Å × 16 Å box was used to simulate the CH\textsubscript{4}, O\textsubscript{2} and CO\textsubscript{2} molecules in the gas phase.

2.8.2. Materials systems.

**Bulk.** The tetragonal unit cell of Mn\textsubscript{3}O\textsubscript{4} made up of 28 atoms was used. This structure was considered since it was shown to be stable experimentally namely in this work and previous
experimental studies. Our calculated bulk lattice parameters $a = b = 5.753 \text{ Å}$ and $c = 9.532 \text{ Å}$ agree well with the those found experimentally $a = b = 5.762 \text{ Å}$ and $c = 9.439$ in Ref. [76], $a = b = 5.765 \text{ Å}$ and $c = 9.442$ in Ref. [72] and $a = b = 5.757 \text{ Å}$ and $c = 9.424$ in Ref. [73]; as well with other values calculated at different level of theory. [74]

**Surface models.** The Mn$_3$O$_4$ (001) surface was considered and modelled using a slab made up of nine alternating –Mn$^{2+}$–Mn$^{2+}$– and –O$^{2-}$–Mn$^{3+}$– layers, the latter being the outermost, followed by a vacuum region of 18 Å in the z-direction were. For adsorption studies, a (2x2x1) supercell with dimensions of 11.51 Å × 11.51 Å × 28.4 Å was considered. All layers were allowed to relax together with the adsorbate molecules. Such a material system was used to describe the interaction of the M$_x$Co$_{3-x}$O$_4$ (001) spinels surfaces (M=Fe, Ni) with water and alcohols, in good agreement with experiment. [75-80]

### 3.8.3. CH$_4$ adsorption and oxidation to CO$_2$

To investigate the oxidation of CH$_4$ to CO$_2$, the adsorption of a single CH$_4$ and its stepwise decomposition into CO$_2$ was computed and analysed via two catalytic routes: the MvK and the L-H mechanisms. At every step, the interaction the reactant molecule and the surface were studied, considering all possible bonding interactions between the molecule and the surface for different starting configurations. Figure 9 (top) and Figure 9 (bottom) show the most stable adsorption geometries and their corresponding binding energies following the MvK and the L-H mechanisms, respectively.

CH$_4$ adsorbs molecularly ontop Mn$^{3+}$ sites via a weak Mn–C bond (2.03 Å) and two weak H-bonds to the surface (2.6 Å and 2.8 Å). Considering the MvK pathway as shown in Figure 10 (top), this results in a binding energy of −0.11 eV. The dissociation via proton transfer to the surface and subsequent formation of CH$_3$ lowers the binding energy and occurs at a cost of 0.08 eV. Further dissociation of CH$_3$ leading to the formation of CH$_2$ is strongly endothermic (1 eV) and corresponds to the determining step. From thereon, all processes are down in energy till the formation of CO$_2$. 

![Figure 9](https://doi.org/10.26434/chemrxiv-2024-p49p5) **ORCID:** https://orcid.org/0000-0003-3622-2716 Content not peer-reviewed by ChemRxiv. **License:** CC BY-NC 4.0
For the Langmuir-Hinshelwood pathway, the presence of ad-oxygens as oxidizing agents renders CH\textsubscript{4} single and double deprotonation into CH\textsubscript{3} and CH\textsubscript{2} exothermic. All decomposition steps are down in energy except for the oxidation of CHO to CO and which correspond to the determining step towards complete oxidation of CH\textsubscript{4} to CO\textsubscript{2}. An energy cost of 0.9 eV is required to overcome this reaction step. This finding supports the key role of ad-oxygen in the oxidation process as also found in previous studies. [81] Our findings suggest that both catalytic pathways could be present during the oxidation of CH\textsubscript{4} to CO\textsubscript{2}. The L-H mechanism could be the most interesting catalytic pathway at low temperatures, while the MvK could occur at higher temperatures.

**Figure 9.**

3.8.4. Electronic structure

Figure 10a-c shows the density of states (DOS), projected on the 3d orbitals of Mn atoms belonging to the bulk and (001) free surface of Mn\textsubscript{3}O\textsubscript{4} respectively. In the case of bulk, the projected DOS of a spin-up polarized Mn atom located in a tetrahedral coordination (Figure 10a) show that, the five spin up orbitals (3d\textsubscript{xy}, 3d\textsubscript{zx}, 3d\textsubscript{zy}, 3d\textsubscript{z}^2 and 3d\textsubscript{x}^2-y^2) are filled, while their spin-down counterparts are empty. The plausible electron configuration for a such atom is [Ar]3d\textsuperscript{5}4s\textsuperscript{0}, which corresponds to the Mn\textsuperscript{+2} ion. However, in the octahedral coordination, the projected DOS of a spin-up polarized Mn atoms show four filled spin-up orbitals (3d\textsubscript{xy}, 3d\textsubscript{zx}, 3d\textsubscript{zy} and 3d\textsubscript{z}^2), one spin-up (3d\textsubscript{x}^2-y^2) and five spin-down (3d\textsubscript{xy}, 3d\textsubscript{zx}, 3d\textsubscript{zy}, 3d\textsubscript{z}^2 and 3d\textsubscript{x}^2-y^2) empty orbitals. For a such atom, the plausible electron configuration is [Ar]3d\textsuperscript{4}4s\textsuperscript{0}, which corresponds to the Mn\textsuperscript{+3} ion (Figure 10b). These observations are in agreement with previous theoretical results. [74]

Regarding the (001) free surface of Mn\textsubscript{3}O\textsubscript{4} (Figure 10c), only the symmetry sites of Mn atoms located on the surface change to square pyramidal, while those deeper atoms remain unchanged (tetrahedral and octahedral) and naturally keep their oxidation states as in the bulk ones. For this reason, we only focus on one square pyramidal site, since all the Mn atoms located on the surface are equivalents. Similarly to the case of a Mn atom in the octahedral site, projected DOS of the spin-up polarized Mn atom located on the free surface, also show four filled spin-up orbitals

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(3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{x^2-y^2}, 3d_{z^2})$, one spin-up (3d_{x^2-y^2}) and five spin-down $(3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{x^2-y^2}, 3d_{z^2})$ empty orbitals. So, the plausible electron configuration for a such atom is [Ar]3d^{4}4s^{0}, which corresponds to the Mn^{3+} ion.

No change on the DOS of Mn atoms located on the surface is observed, neither when the CH_{4} molecule is adsorbed (Figure 9d), nor when oxidation occurs via Mars-van-Krevelen (Figure 10e) and the Langmuir-Hinshelwood (Figure 9f) mechanisms. Thus, the oxidation state of surface Mn atoms remains unchanged regardless the mechanisms that is taking place on the surface.

Figure 10.

3.9. Stability on time-on-stream of CH_{4} Oxidation over Mn_{3}O_{4}

The long-term stability test is on the crucial catalysts criteria required for an industrial application. Herein, Mn_{3}O_{4} on prolonged stream time-on-stream (TOS) was carried out and presented in Figure 11. The experiment was conducted following the catalytic test condition; however, the date was recorded when the reaction temperature reached ~498 ◦C, a temperature at which ~90% conversion of CH_{4} over Mn_{3}O_{4} was achieved. Figure 9 reveals that the conversion was constant at ~90% within the first 100 min, then shifted gradually up to ~80%. The stability on TOS of 1 Mn_{3}O_{4} SPs is decreased, due to the coverage of the active sites by soot particles or H_{2}O vapor that prohibit CH_{4} and O_{2} adsorption onto Mn_{3}O_{4} surface. In addition, the presence of chemically less active -OH group adsorbed at the Mn_{3}O_{4} surface over lattice oxygen is reported to decline in the performance TMOs catalysts. [82,83]

Figure 11.

4. Conclusions

Mesoporous Mn_{3}O_{4} catalysts with spherical-like particles have been successfully synthesized by the sol-gel technic and tested as for the methane catalytic combustion. The comprehensible characterization results utilizing XRD, FTIR, S_{BET}, XPS, SEM, and H_{2}-TPR technics showed that the outstanding performance of the Mn_{3}O_{4} SPs is crucially rely to its larger surface area, narrow particles sizes, the presence of Mn^{4+}, and the excellent low-temperature
reducibility. Mn$_3$O$_4$ has been effectively investigated as catalyst for total conversion of methane to CO$_2$ and H$_2$O. CH$_4$ oxidation over Mn$_3$O$_4$ revealed the occurrence of both the MvK and L-H mechanisms, and the latter is more ascendant. In this concerted and cooperative process, the rate-determining step is CH$^*$ dehydrogenation to H$^*$. Besides, the Mn$_3$O$_4$ nano-sphere catalyst can keep significant stability at 400 °C for more than 16 h, attesting of the prominent performance towards methane total conversion. This work demonstrates that the structure-related catalytic performance could guide in the further development low-cost TMOs based catalysts and their derivatives for CH$_4$ total oxidation.

4. Experimental

4.1. Chemicals

Manganese (II) sulfate monohydrate (MnSO$_4$.H$_2$O), sodium persulfate (Na$_2$S$_2$O$_8$), and ethanol were procured from Sigma Aldrich Pty Ltd., (Hamburg, Germany). NaOH solution was prepared from Na$_2$S$_2$O$_8$ in deionized water, and obtained by using an ultra-pure purification system.

4.2. Catalysts Synthesis

Mn$_3$O$_4$ (NSs) catalyst was synthesized by sol-gel method employing manganese (II) sulfate monohydrate as metal precursor. MnSO$_4$.H$_2$O (3g) were dismissed in 35 mL of distilled water under vigorous stirring with the magnetic stirrer for 10 minutes. Then, 15 mL of the initially prepared NaOH was added in drops under strong magnetically stirring until pH = 9 for about 30 minutes at a fixed temperature of 60 °C. The obtained precipitate phase was filtered and washed with distilled water and overnight in an oven at 100 °C. Finally, the precipitate was thermally treated at 400°C for 2 hours to obtain Mn$_3$O$_4$ nanoparticles as the final product.

4.3. Characterization section

The Mn$_3$O$_4$ SPs crystal structure and phase was studied by the X-ray diffraction (XRD) analysis. The analysis was performed on an X-ray diffractometer equipped with a powder diffraction tools using Bruker Cu Kα radiation operating with $\lambda = 0.154056$ nm, D8 Focus fixed at 40 kV under 150 mA. The values of 2θ were ranged from 20 to 70° and was chosen as the recording range of the
Mn₃O₄ sample, for a scanning speed of 0.025° per second. The resulting spectrum was ascertained by comparing with the JCPDS (Joint Committee on Powder Diffraction Standards) database.

To determine the grain size diameter of the Mn₃O₄ NSs, the equation of Debye Scherrer was applied (Equation 2):

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

(2)

In which, D represents the average size of the crystallites, k corresponds to the shape factor (0.9), \( \lambda \) is the wavelength, \( \beta \) represents the line broadening, and finally \( \theta \) is the diffraction angle.

The specific surface area (SBET) of the samples was measured using Brunauer–Emmett–Teller (BET) approach on N₂ physisorption equipment (NOVA3000, Quantachrome) and calculated through BET equation. Prior to the analysis, the thermally treated Mn₃O₄ SPs were heated at 250 °C under vacuum for 3 h to remove H₂O and CO₂, after a nitrogen was adsorbed at ~196 °C and desorbed at ambient temperature. Fourier transformed infra-red (FTIR) spectroscopy (Perkin-Elmer), was applied to identify functional groups at the surface of the catalyst in the wave numbers region varying from 4000 to 400 cm⁻¹. The surface structure and morphology of the Mn₃O₄ SPs was carried out at ambient temperature using high-resolution SEM equipment (S-4800 Hitachi, USA).

To confirm the availability of Mn and O atoms and their oxidation states, X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was employed. To evaluate the reducibility of Mn₃O₄ NSs, the temperature-programmed reduction under dihydrogen flow (H₂-TPR) was performed using a chemical adsorption equipment (PCA-1200, Pekin Builder) associated with a quartz reactor and a thermal conductivity detector (TCD) detector.

4.4 Catalytic test investigation

Methane total oxidation over Mn₃O₄ SPs was investigated in a stainless-steel fixed bed reactor system with tubular form (internal Ø, 6 mm). The light-off measurements were performed with 60 mg of catalyst dispersed on 40-60 mesh, enrolled, and disposed at the reactor center. The reactants inlet was composed of 1% CH₄ and 20% O₂ diluted in an Ar flow, and the total gas pressure was maintained at 1 atm. The reaction was performed at 60 mL.min⁻¹ (total flow rate), equivalent to a
gas hourly space velocity (GHSV) of 72 000 mL$^3$.g$^{-1}$.h$^{-1}$ and within the temperature range of 100 to 550°C. The temperature inside the reactor was controlled by a k-thermocouple disposed at the reactor center in direct contact with the catalyst bed. The inlet and outlet gas were quantitatively monitored online via a gas chromatograph (GC-2014, Shimadu) coupled with a flame ionization (FID) and TCD detector. The CH$_4$ abatement was determined using the relationship in Equation 3:

\[
\text{CH}_4 = \frac{\text{CH}_4\text{input} - \text{CH}_4\text{output}}{\text{CH}_4\text{input}}
\]  

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Conflicts of Interest

The authors declare no conflict of interest.

Data availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References


Table caption

Table 1: Comparison of the sol-gel derived Mn₃O₄ catalytic efficiency (T₅₀, T₉₀) to that of the selected catalysts from the literature

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Weight (mg)</th>
<th>Gas inlet</th>
<th>¹WHSV (mL³.g⁻¹.h⁻¹)</th>
<th>²T₅₀</th>
<th>³T₉₀</th>
<th>Mechanism</th>
<th>³Ref.</th>
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</thead>
<tbody>
<tr>
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<td>60</td>
<td>1% CH₄, 20% O₂ in Ar</td>
<td>72 000</td>
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<td>398</td>
<td>MvK</td>
<td>TW</td>
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<tr>
<td>Co₃O₄</td>
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<td>1% CH₄, 10% O₂</td>
<td>60,000</td>
<td>330</td>
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<td>463</td>
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<td>364</td>
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<tr>
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<td>313</td>
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<tr>
<td>Pd/Zr₀.₆₅Ce₀.₃₅O</td>
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<td>75,000</td>
<td>344</td>
<td>398</td>
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<td>[55]</td>
</tr>
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</table>

¹WHSV=Gas hourly space velocity; ²T₅₀ and ³T₉₀: Temperature at 50 and 90 % conversion; ³Ref.: references
Figures captions

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