Integrated In Situ Characterization of a Molten Salt Catalyst Surface: Evidence of Sodium Peroxide and Hydroxyl Radical Formation

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Supporting Information
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Experimental Procedures

**Catalyst preparation**: The Na$_2$WO$_4$/SiO$_2$ and Na$_2$WO$_4$/TiO$_2$ catalysts were prepared with a conventional wet impregnation method using Na$_2$WO$_4$·2H$_2$O (Sigma-Aldrich), SiO$_2$ (Sigma-Aldrich, Silica Gel, Davissil Grade 646, 35–60 mesh, 300 m$^2$ g$^{-1}$) and TiO$_2$ (Evonik, P25, 50 m$^2$ g$^{-1}$).

**Catalytic test**: The rates and selectivities of the CH$_4$/O$_2$/H$_2$O reactions were measured using flow reactors and a U-shaped quartz cell (4 mm I.D.). The samples (0.02 g) were held on quartz wool without dilution. The temperature was maintained using a Honeywell controller coupled to a resistively heated furnace and measured with a K-type thermocouple placed outside the catalyst bed. CH$_4$ (99.9995%), 20% O$_2$ in He, and He (99.999%) were purchased from Abdullah Hashim Industrial Gases & Equipment Co., Ltd. (AHG) and used after further purification by filtration. The flow was regulated by mass flow controllers. A saturator with a well-controlled temperature (5–20°C) was used to introduce the H$_2$O gas. The reactant and product concentrations were measured using a VARIAN gas chromatograph 450GC with a programmed system that was equipped with a molecular sieve 5 Å column, a HayeSep Q column with a thermal conductivity detector and a VARIAN CPWax 52 CB capillary column with a flame ionization detector. This configuration enables the differentiation of all C$_1$–C$_4$ hydrocarbons. For H$_2$ detection, a micro-gas chromatograph (Agilent Technologies 3000A) equipped with thermally conductive molecular and plot U columns was used.

**Laser-induced fluorescence (LIF) spectroscopy for OH radical detection**: A schematic representation of the experimental setup and actual photos are shown in Figure S1. The hydroxyl radicals (OH) formed on the catalyst surface were detected approximately 2 mm above the surface of the alumina boat containing the catalyst. Laser-induced fluorescence (LIF) was utilized to detect the formed hydroxyl radicals. The excitation of the OH radicals was carried out using a frequency-doubled tunable dye laser (continuum, ND 6000) pumped with a frequency-doubled Nd:YAG laser (Continuum, Powerlite DLS), as shown in Figure S1. The dye laser produced a fundamental beam at 566 nm with Rhodamine 590 dye. Then, this light was frequency doubled using a frequency double unit (Continuum, UVT-3) to produce an ultraviolet beam at 283 nm. The laser wavelength was tuned to 282.93 nm to pump the Q$_1$(6) transition (1,0) in the band of $A^2\Sigma^+ ← X^2\Pi(1,0)$ OH system. The laser produced 0.3 mJ/pulse at 283 nm with a pulse width of 5 ns at a repetition rate of 10 Hz. The laser beam was transformed and focused using telescopic cylindrical lenses to the test section inside the furnace. The LIF images were acquired at a 90° angle to the laser beam using an intensified charge-couple device (ICCD) camera (Princeton Instruments, PI-MAX3 1024i), which was equipped with Nikkor UV lenses (f/4.5, f = 105 mm) and appropriate filters. A transmission bandpass interference filter with a transmission range of 295-345 nm (> 80% at 310 nm) (custom fabrication-Laser-Components GmbH) was used to achieve good discrimination of the OH excitation. To reduce the effect of the background, the images were captured with a 20-ns camera gate width and 70% gain. A TTL signal from a delay generator (SRS, FG535) triggered the ICCD camera and the pumping Nd:YAG laser.

![Figure S1](image-url)  
*Figure S1*. Schematic representation and photographs of the experimental setup used for OH radical detection.
In situ X-ray diffraction (XRD) measurement: The XRD measurement was performed in the θ-2θ configuration using a Bruker D8 discovery diffractometer (Cu Kα₁ radiation) in the 10° to 80° range with a 0.02° step size and 0.4 s counting time per step. The experiments were conducted in situ at various temperatures (up to 800°C) under an air atmosphere. The temperature was controlled by a Paar HKT 1200 system. The temperature was increased from room temperature (25°C) to 800°C at a rate of 20°C min⁻¹.

In situ scanning transmission electron microscopy: The STEM images were recorded using an FEI Titan ChemiSTEM that operated at 200 kV with a beam current of 100 pA and a convergence angle of 19 mrad at North Carolina State University’s Analytical Instrumentation Facility. The TEM was equipped with a Protochips Atmosphere Gas E-cell, which uses a pair of silicon-based MEMS devices to create a small cell inside the tip of the Atmosphere TEM holder. The NaWO₄/TiO₂ samples were deposited from a methanol suspension after crushing with a mortar and pestle and sonicating onto a MEMS heating device and loaded into the Atmosphere holder. The sample was exposed to 1 atm of air (grade 0.1, ARC3 gas supply) in flowing mode and temperatures between 150°C and 900°C. Energy dispersive X-ray spectroscopy (EDS) analysis was performed using a Titan ChemiSTEM equipped with a SuperX EDS system.

Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS): The catalyst sample was loaded on Au foil via a drop-casting method followed by mounting in an in situ reaction cell of an UHV chamber. The reaction cell is integrated with a monochromated Al K-alpha X-ray source and energy analyzer. The mixture of reactant gases was introduced into the reaction cell through a gas manifold, where all the reactant gases were mixed and the pressures were measured. All the gases used (CH₄, O₂, He) for the AP-XPS studies were purchased from Matheson at a purity of 99.99% or higher. Typically, the total flow rate of the mixture of the pure reactant gases in the reaction cell was approximately 4 mL min⁻¹. First, the Na1s, O1s and W4f photoemission features were collected at UHV and 20°C. Then, the sample was heated to 800°C under a flow of 0.5 Torr oxygen and 0.5 Torr deionized water vapor. For the second test, fresh catalyst was mounted and investigated at 20 and 800°C under 0.5 Torr O₂ with 0.5 Torr CH₄. The XPS data was analyzed using CasaXPS software. All the spectral peaks were calibrated using Au 4f₇/₂. However, a thermal shift in the binding energy was observed at high temperature. Because O1s of Na₂O₂ and O1s of Na₂WO₄ have similar binding energies and their peaks are very sharp, we can align the O1s collected under different conditions to the same binding energy, by which we can align other peak positions. This alignment is supported by the same binding energy of Ti3p of TiO₂ at different experimental conditions after the alignment.
Results and Discussion

Catalytic results. The CH₄/O₂ reaction on Na₂WO₄/TiO₂ was performed in a plug-flow reactor with a temperature-regulated H₂O saturator. Figure S2a shows the CH₄ conversion when the H₂O partial pressure (0-2.3 kPa) was varied at constant CH₄ and O₂ pressures (20 and 5.6 kPa, respectively). The CH₄ conversion increased with increasing H₂O pressure, which is consistent with H₂O involving CH₄ activation.

\[ r = k_{\text{cat}} + k_{\text{ads}} = k_{\text{CH₄}}P_{\text{CH₄}}^{0.5} + k_{\text{O₂}}P_{\text{O₂}}^{0.5}P_{\text{H₂O}}^{0.5} \]  

(1)

In the absence of O₂, CH₄/H₂O did not result in CH₄ conversion, indicating that the catalyst does not catalyze steam reforming, and O₂ is essential for CH₄ activation. Figure S2b shows the CH₄ conversion rate as a function of \( P_{\text{O₂}}^{0.5}P_{\text{H₂O}}^{0.5} \), which exhibits a linear correlation that suggests that CH₄ reacts with quasi-equilibrated OH radicals based on Eq. (1). Similarly, the kinetic relationship was sustained at various O₂ and H₂O pressures (extracted for the second term in Eq. (1)), as shown in Figure S2c. The wet condition not only improves the rate but also the selectivity, as shown in Figure S2d. This result is consistent with the kinetic explanations for improved selectivity via an OH radical pathway. These kinetic results are consistent with those in our previous studies, where Na is an essential component for this OH radical reaction pathway, and W helps to immobilize Na.

At higher conversions where \( \text{O₂/H₂O} \) ratio becomes very small, our previous study showed that irreversible O₂ chemisorption becomes kinetically relevant step as shown in Eq. (2).

\[ r = k_{\text{O₂}}P_{\text{O₂}} \]  

(2)

Even under this kinetic regime, the OH radical pathway, or wet rate, \( r_{\text{cat}} \), generally contributes more than the surface O* pathway, or the dry rate, \( r_{\text{O₂}} \), making water effects essential to achieve high OCM selectivity regardless of conversions.

Figure S2. Catalytic results for the CH₄/O₂/H₂O reaction using the Na₂WO₄/TiO₂ catalyst (30 mg, 800°C, 20 kPa CH₄, 3.0-8.3 kPa O₂, 0-2.3 kPa H₂O, total pressure 101 kPa balanced by He, total flow rate 25 cm³ min⁻¹). (a) CH₄ conversion as a function of the H₂O pressure. (b) CH₄ conversion rate as a function of the \( P_{\text{O₂}}^{0.5}P_{\text{H₂O}}^{0.5} \). (c) Incremental CH₄ conversion rate \( \Delta r_{\text{CH₄}} \) (rate difference between the presence and absence of H₂O) as a function of the \( P_{\text{O₂}}^{0.5}P_{\text{H₂O}}^{0.5} \). (d) O₂+ selectivity as a function of the H₂O pressure.
**Figure S3.** In situ XRD patterns of Na$_2$WO$_4$/TiO$_2$ catalyst before and after pretreatment at 900°C in flowing air for 15 h (top) and at various temperatures in an air atmosphere (bottom). Time course appears from bottom to top of the patterns. A final record was made at 25°C after 3 h.

**Figure S3** shows the XRD patterns of the Na$_2$WO$_4$/TiO$_2$ catalyst before and after pretreatment at 900°C (top), during a heating process from 25 to 800°C, and a cooling process down to 25°C (bottom). After impregnation of Na$_2$WO$_4$, TiO$_2$ phase was mainly anatase, which was transformed into rutile after pretreatment in flowing air at 900°C (Figure S3, top). Before heating, the pattern at room temperature (Figure S3, top and Figure S3, bottom “initial at 25°C”) exhibits peaks corresponding to the TiO$_2$ rutile phase and Na$_2$WO$_4$ cubic phase. Indeed, Na$_2$WO$_4$ crystallizes as the cubic phase with a lattice constant of $a = 9.13$ Å for $T < 597.6^\circ$C. However, at higher temperatures, Na$_2$WO$_4$ crystallizes in the orthorhombic phase with lattice parameters of $a = 7.72$ Å, $b = 10.07$ Å, and $c = 5.58$ Å. At 500°C, the pattern did not change. By increasing the temperature to 700°C, the Na$_2$WO$_4$ cubic phase disappeared, and the TiO$_2$ rutile phase remained unchanged, which indicated that Na$_2$WO$_4$ melted. A similar XRD pattern was obtained at 800°C. For cooling to 600°C, the XRD pattern corresponds to the TiO$_2$ rutile phase with new peaks due to the Na$_2$WO$_4$ orthorhombic phase. When the cooling process was continued down to 25°C, the peaks for the Na$_2$WO$_4$ orthorhombic phase disappeared, while those for the cubic Na$_2$WO$_4$ phase began to appear. After 3 h and exposure to ambient conditions, the original Na$_2$WO$_4$ cubic phase was completely recovered.
Figure S4. An ex-situ Raman spectrum of Na$_2$WO$_4$/TiO$_2$ catalyst after pretreatment at 900°C in flowing air for 15 h, and two reference Raman spectra of TiO$_2$-rutile powder and Na$_2$WO$_4$ powder.
Figure S5. Thermogravimetric analysis and differential scanning calorimetric analysis in air (Sample: Na$_2$WO$_4$·2H$_2$O, Weight: 50.74 mg, Air flow rate: 100 ml min$^{-1}$, ramping and cooling rates, 10°C min$^{-1}$).

Figure S5 shows the thermogravimetric analysis combined with differential scanning calorimetry of unsupported Na$_2$WO$_4$·2H$_2$O (supported catalyst did not exhibit any change due to extremely small loading: 0.6 wt% Na). Slightly above 100°C, the weight loss associated with an endothermic reaction occurred, indicating a dehydration reaction. After this initial weight change, the weight remained nearly unchanged during the heating and cooling procedure. In contrast, endothermic peaks were observed at ~600°C and ~700°C, which were due to a crystal phase change from cubic to orthorhombic and fusion, respectively. Two exothermic peaks were observed during the cooling process. The crystal phase transition coincides with the XRD behavior at ~600°C during cooling.
Figure S6. Energy dispersive spectroscopy image in STEM mode.
Figure S7. XPS Au 4f collected from Au foil-supported catalyst particles at UHV and 20°C (black line), 66 Pa O₂ and 66 Pa H₂O at 800 °C (red line), 66 Pa O₂ and 66 Pa CH₄ at 20°C (blue line), and 66 Pa O₂ and 66 Pa CH₄ at 800°C (pink line).
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Author Contributions

K.T. and A.M.K. conducted the catalytic studies. Y.T., L.N. and F.T. performed the AP-XPS. K.T. and A.Z. conducted the in situ XRD measurements. B.W.J. conducted the in situ TEM. K.T., A.M.E. and S.M.S. conducted the LIF OH radical detection experiment. K.T. A.M.E., S.M.S. and F.T. wrote the manuscript. K.T. supervised the entire project. All authors reviewed the manuscript.