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Systematic exploration of alkali–anion pairs for descriptor identification in OH-mediated methane coupling†

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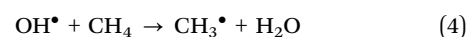
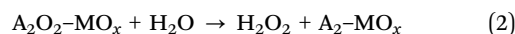
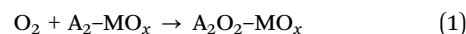
The oxidative coupling of methane (OCM) was investigated using various alkali metal salts supported on SiO₂. The addition of H₂O enhances both the methane conversion rate and selectivity across all alkali metal salts, which suggests there is an OH-radical-mediated pathway that is facilitated by the surface formation of alkali peroxide. To explain the observed experimental differences, we explored the interactive energetics of alkali–anion pairs with a particular focus on the stabilization of alkali peroxide intermediates by anion species. Anion polarizability is indicative of the alkali ion's degree of freedom and positively correlated with the catalytic performance due to formation capability of catalytic alkali peroxide species. This insight highlights the critical role of the reaction of surface alkali peroxide with H₂O as a key elementary step in OCM.

The oxidative coupling of methane (OCM) involves the reaction of CH₄ directly with O₂ at high temperatures (> ~600 °C) to produce C₂ products (C₂H₆, C₂H₄) over heterogeneous catalysts.¹ The design of relevant catalysts is centered around improving selectivity to C₂ products over CO_x (CO₂, CO). C₂ formation occurs via the gas-phase coupling of CH₃ radicals² with CH₃ generated on the catalyst surface. Thus, the integration of surface and gas-phase reactions is required to describe the reaction adequately.^{3–5}

Supported alkali metal tungstate catalysts stand out for having the highest selectivity towards C₂ products since the first reports of Mn–Na₂WO₄/SiO₂.⁶ Various reports have argued that WO₄^{2–} acts as the CH₃ formation site. However, the reported mechanisms vary and have included the involvement of WO₄^{2–} lattice oxygen,^{7,8} surface-derived O₂[–],^{9,10} and surface NaWO_x species.^{11,12} The roles of both Na¹³ and Mn¹⁴ have been reported to involve the distortion of the WO₄^{2–} centers. In addition, H₂O is known to have a promotional effect by accelerating CH₄ conversion and improving C₂ selectivity,¹⁵ which

complicates the kinetic analysis. Zanina *et al.* suggested that H₂O has a role in the removal of CO_x-selective peroxide-type O₂ surface species.^{8,16} However, Wang *et al.*¹⁷ reported that surface O₂ species selectively form C₂ products, while Liu *et al.*¹⁸ attributed the H₂O effect to the formation of Si–OH surface species.

Our research group has argued that the selective formation of CH₃ radicals involves OH-radical intermediates that are generated by H₂O and O₂ reacting on the Na sites of the catalyst surface (possibly from H₂O₂ release).¹⁹ This mechanism can be described by the following:



where A is the alkali cation, and A_xMO₄ represents the bulk catalyst. Gas phase reactions (3)–(5) have been demonstrated to be C₂ selective,²⁰ although H₂O₂ has not been observed directly.

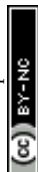
Alkali metal peroxide intermediates have been observed by near-atmospheric-pressure X-ray photoelectron spectroscopy (XPS) on K₂WO₄²¹ and Na₂WO₄²² catalysts, and OH radical generation has been observed using laser fluorescence. Alkali metal peroxides are expected to be the key surface intermediate and likely generate either OH radicals directly or H₂O₂,²³ which subsequently decomposes into two OH radicals (eqn (2)). Thus, the catalyst's effectiveness will depend on the presence of an alkali metal salt, regardless of the identity of the cation or anion.

Systematic modification of alkali metal cations is common in the catalytic literature.^{24,25} Zanina *et al.* investigated the effect of the identity of the alkali metal cation,^{26,27} and Palermo *et al.*²⁸ confirmed that various alkali metals can be effective for OCM. In addition, studies have been conducted on the effects of changing the anion. Supported alkali metal MoO₄^{2–} has been shown to be effective for OCM (LiCl–Na₂MoO₄),²⁹ partial CH₄ oxidation ((Li, Na, K, Rb, Cs)₂MoO₄/SiO₂),³⁰ and nonoxidative

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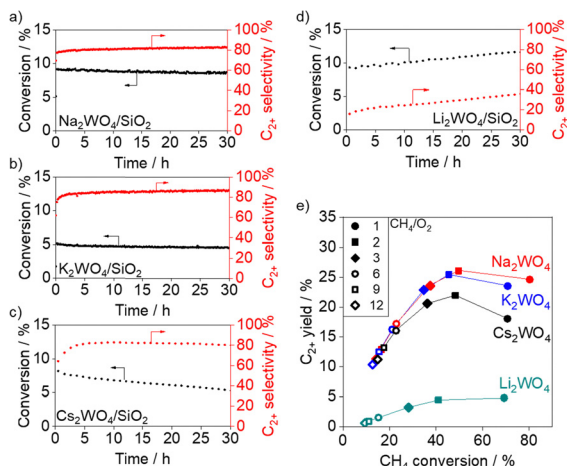


Fig. 1 CH₄ conversion and C₂₊ selectivity as a function of time on stream for (a) Na₂WO₄/SiO₂, (b) K₂WO₄/SiO₂, (c) Cs₂WO₄/SiO₂, and (d) Li₂WO₄/SiO₂ at 850 °C with 10 kPa CH₄ and 1.7 kPa O₂ (balance Ar) using 0.1 g catalyst and 30 mL min⁻¹ flow. (e) Maximum achievable C₂₊ yield as a function of CH₄ conversion at varying CH₄/O₂ ratios (maintaining 10 kPa CH₄ and adjusting O₂ pressure). Detailed results are summarized in Table S1 (ESI†).

CH₄ aromatization (K₂MoO₄/ZSM-5).³¹ Both Na₂SO₄/SiO₂³² and K₂MnO₄/SiO₂³³ have also been shown to be effective for OCM, with the latter showing a promotional effect of H₂O. A systematic modification of the metal anion was conducted by Hou *et al.* on Mn-promoted Na-salts which focused on the anion–Mn interaction.³⁴ Both variables need to be examined to accurately determine the kinetic impact of varying cation and anion species in the alkali metal salt catalysts.

The aim of the present study was to fill the gaps in the research by examining a wide variety of alkali metal salt catalysts for OCM with a focus on the promotional effect of H₂O. The OCM reaction rate and selectivity were measured using a fixed-bed plug flow reactor (PFR) with a U-shaped tube. Fig. 1 shows the CH₄ conversion rate and C₂₊ selectivity (including hydrocarbons larger than C₂) as a function of time on stream for M₂WO₄/SiO₂ catalysts (where M represents Li, Na, K, or Cs) at 850 °C and a CH₄/O₂ ratio of 6. For the cations Na, K, and Cs, the CH₄ conversion decreased over time, while C₂₊ selectivity increased. The decrease in CH₄ conversion rate can result from either sintering of the catalyst or the desorption of the active M₂WO₄, which reduces the number of active sites. Cs₂WO₄/SiO₂ showed lower durability than the other catalysts, likely due to the low melting point (350 °C) of Cs₂WO₄ compared to Na₂WO₄ (698 °C) and K₂WO₄ (921 °C). In contrast, Li₂WO₄/SiO₂ showed increases in both the CH₄ conversion and C₂ selectivity over time, but the C₂ selectivity was much lower.

The maximum achievable C₂₊ yield was achieved at a CH₄/O₂ ratio of 2 for most samples, as is shown in Fig. 1e. Both Na₂WO₄/SiO₂ and K₂WO₄/SiO₂ showed similar obtainable C₂₊ yield, with Na₂WO₄ reaching 26.1%. Cs₂WO₄/SiO₂ showed similar results but had a lower yield due to the lower selectivity towards C₂₊ products, particularly at lower CH₄/O₂ ratios. This indicates a higher tendency towards product oxidation. Li₂WO₄/SiO₂ showed

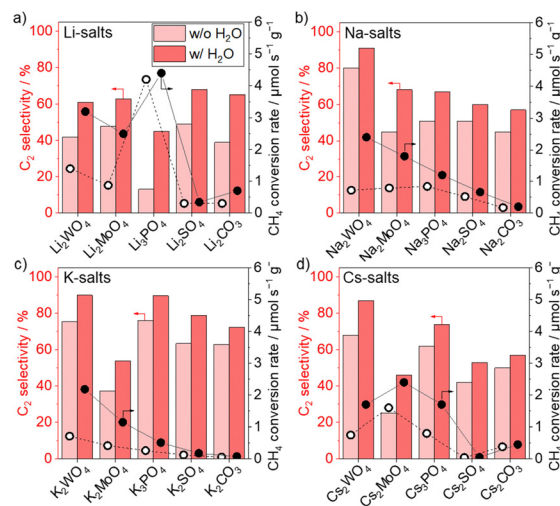


Fig. 2 CH₄ conversion rate and C₂ selectivity of (a) Li-salt catalysts, (b) Na-salt catalysts, (c) K-salt catalysts, and (d) Cs-salt catalysts on SiO₂ for OCM at 850 °C with 10 kPa CH₄ and 1.7 kPa O₂ (balance Ar) using 0.2 g catalyst and 30–150 mL min⁻¹ flow extrapolated to 1% CH₄ conversion. Detailed results are listed in Table S2 (ESI†).

significantly lower C₂₊ yield and only reached 4.8% at a CH₄/O₂ ratio of 1. This was clearly due to the low selectivity of this catalyst compared to the other alkali metal tungstate catalysts.

Next, various cations (Li, Na, K, and Cs) were introduced with various anions (WO₄²⁻, MoO₄²⁻, SO₄²⁻, PO₄³⁻, and CO₃²⁻) and tested for their OCM performance. Alkali metal salts (5 wt%) on SiO₂ were prepared using the wet impregnation method. Fig. 2 shows the C₂ selectivity and CH₄ conversion rate for each catalyst. Alkali metal salts were expected to remain on the surface of the SiO₂ based on observation of XPS (Fig. S1–S16, ESI†). The results were measured at 850 °C with 1% CH₄ conversion, 10 kPa of CH₄, and 1.7 kPa of O₂ (CH₄/O₂ = 6) with either 1.7 kPa H₂O (wet) added at the inlet or without H₂O addition (dry). The WO₄²⁻ anion, particularly with Na₂WO₄/SiO₂ and K₂WO₄/SiO₂, showed the best C₂ selectivity with high CH₄ conversion rates. The MoO₄²⁻ anions also showed high CH₄ conversion rates but were limited by low C₂ selectivity. The SO₄²⁻, PO₄³⁻, and CO₃²⁻ anions typically showed significantly lower CH₄ conversion rates.

The alkali metal also showed an impact on the OCM performance. Na⁺ and K⁺ typically had higher C₂ selectivity, and Li⁺ showed lower C₂ selectivity. However, all catalysts showed a clear promotional effect of H₂O for C₂ selectivity and CH₄ conversion. Although the promotional effect is unique to alkali metal salts, all instances of them universally show H₂O promotion, which is a strong indicator that these catalysts share a similar reaction mechanism.

The catalysts showed a wide range of physical properties after the initial synthesis and calcination at 900 °C. The measured surface areas (Table S3, ESI†) were 0.7–32 m² g⁻¹. Much of the loss of surface area was due to transformation of amorphous SiO₂ into the cristobalite phase, which was catalyzed by the alkali metals (Table S4, ESI†). However, some catalysts were not able to fully transform the SiO₂, and it remained amorphous (Table S4 and Fig. S17, ESI†). This is known to decrease C₂



selectivity. In addition, the catalyst loading measured by atomic adsorption spectroscopy (AAS) and inductively coupled plasma (ICP) had a wide range. Samples with the CO_3^{2-} anion showed the largest loss of catalyst content due to thermal decomposition (Table S4, ESI†).

In contrast, the ratio of CH_4 conversion under wet conditions to that under dry conditions ($r_{\text{wet}}/r_{\text{dry}}$) should be relatively unaffected by textural and metal loading differences. The value of $r_{\text{wet}}/r_{\text{dry}}$ should directly correlate to the catalyst's capacity towards the OH-radical-mediated pathway, in addition to the overall effectiveness of the catalyst. The $r_{\text{wet}}/r_{\text{dry}}$ is also insensitive to the loss of catalyst species during the high temperature reaction. $\text{Cs}_2\text{WO}_4/\text{SiO}_2$ showed a similar C_2 selectivity to $\text{Na}_2\text{WO}_4/\text{SiO}_2$ at low conversion, whereas at high conversion (Fig. 1e), $\text{Cs}_2\text{WO}_4/\text{SiO}_2$ showed much lower performance, which can be correlated to a lower $r_{\text{wet}}/r_{\text{dry}}$ for this catalyst. When considering the OH-radical-mediated pathway, the first step in the reaction was postulated to be the formation of an alkali peroxide from the surface alkali metal oxide according to eqn (1). Therefore, alkali metal peroxide formation is critical to the OCM performance.

The order of the $r_{\text{wet}}/r_{\text{dry}}$ results (and thus the OH radical formation ability) can be related to several physical properties of the anion species. Fig. 3 shows $r_{\text{wet}}/r_{\text{dry}}$ as a function of the formation energy for each alkali metal. The $r_{\text{wet}}/r_{\text{dry}}$ ratio generally increased with increasing formation energy. In addition, the relative effectiveness of the anion can be clearly seen, and the highest H_2O promotion was observed in the order of $\text{WO}_4^{2-} > \text{MoO}_4^{2-} > \text{PO}_4^{3-} > \text{SO}_4^{2-}$.

A selection of physical properties of anions is shown in Table 1. The polarizability of WO_4^{2-} and MoO_4^{2-} were not directly tabulated in the literature, but estimates were obtained from reported dielectric factors (see ESI† for details, Table S5). The anionic radii and polarizability increased in order of $\text{WO}_4^{2-} > \text{MoO}_4^{2-} > \text{PO}_4^{3-} > \text{SO}_4^{2-}$, which tracks with the order of $r_{\text{wet}}/r_{\text{dry}}$. Both the anionic radius and polarizability correlate to the relative flexibility of the anion. Larger anions will have a lower average charge density and thus have higher

Table 1 Chemical properties of anion species

Anion ^a	Ionic radius/pm ^a	Polarizability/ $\text{\AA}^3$ ^a	pK_a ^d
WO_4^{2-}	237	9.9–10.0 ^b	3.6–5.1 ^e
MoO_4^{2-}	231	6.7–8.1 ^b	4–4.2 ^f
PO_4^{3-}	230	6.8 ^c	2.2
SO_4^{2-}	218	5.1 ^c	–3

^a Values obtained from Simoes *et al.*³³ ^b Estimated from dielectric factor, see ESI for details. ^c Obtained from Hou *et al.*³⁴ ^d Reported pK_a values of H_xMO_4 . ^e Values obtained from Li *et al.*³⁵ ^f Values obtained from Goldberg.³⁶

polarizability. The increase in polarizability allows for dispersion of the negative charge on the anion. The distributed charge allows for the anions to be distorted more easily. In addition, the reported pK_a values of the corresponding protonic acids (H_xMO_4 ; Table 1) increase with $r_{\text{wet}}/r_{\text{dry}}$. The pK_a values correlate with the decreases in relative acidity with increasing ion radius, although it was measured in very different conditions (aqueous phase, room temperature) than those used for OCM. However, there is still a clear relationship between these parameters and the OH radical formation ability of the catalysts.

The properties of the anions listed in Table 1 are related to the relative structural degree of freedom according to the anion species. The alkali (su)peroxide species are highly unstable and even volatile under OCM condition. Stronger bonds between cation–anion species allow the alkali metal to stay on the surface of the catalyst, which limits the range of available positions to form peroxide surface intermediate species. A flexible anion allows for higher alkali metal mobility, which is likely to allow for O_2 chemisorption and the formation of alkali metal peroxide bonds. Intuitively, heavier anions (WO_4^{2-} , MoO_4^{2-}) have higher polarizability than the lighter anions (PO_4^{3-} , SO_4^{2-}), which helps to explain why these anions are typically the only ones viable for OCM. WO_4^{2-} shows much larger polarizability than the other anions, in addition to a distinctively large value of $r_{\text{wet}}/r_{\text{dry}}$.

The cations are the active sites in the OH radical mechanism, and their effect was also investigated. The critical step of the reaction is the formation of the alkali metal peroxide (A_2O_2), so the values of $r_{\text{wet}}/r_{\text{dry}}$ were correlated to the A_2O_2 formation energy from the alkali metal oxide (A_2O , Fig. S18, ESI†). The highest $r_{\text{wet}}/r_{\text{dry}}$ value of WO_4 -related catalysts occurred with Na and K, reaching 2.5 and 2.7, respectively. Both Na_2O_2 (-98 kJ mol^{-1}) and K_2O_2 (-133 kJ mol^{-1}) have moderate formation energies compared to Li_2O_2 (-34 kJ mol^{-1}) and Cs_2O_2 (-311 kJ mol^{-1}). If the formation energy is too low, it will limit the stability of A_2O_2 and decrease the overall rate. If it is too high, it will over-stabilize the A_2O_2 and limit further reaction to form either H_2O_2 or OH radicals. However, this correlation is only observed with WO_4 and loosely with SO_4 . MoO_4 showed the highest $r_{\text{wet}}/r_{\text{dry}}$ on $\text{Li}_2\text{MoO}_4/\text{SiO}_2$, while PO_4 showed the highest with $\text{Cs}_3\text{PO}_4/\text{SiO}_2$. In addition, the cation effect was much weaker in comparison to the observed anion effect. The nature of the anion is clearly more important for the OCM performance than the nature and identity of the alkali metal cations.

Direct observation of the alkali metal salt bonding was attempted, but it was difficult due to the gap between OCM

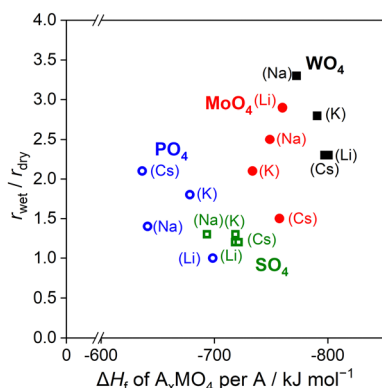


Fig. 3 Ratio of wet (1.7 kPa H_2O added) over dry (no additional H_2O) CH_4 conversion rate as a function of formation enthalpy of the catalyst salt. Rates were determined at 1% CH_4 conversion and 850°C with 10 kPa CH_4 , 1.7 kPa O_2 , and balance Ar.



conditions and available characterization techniques. XPS (Fig. S19, ESI†) was used to observe binding-energy differences on either the alkali metal (Li, Na, K, or Cs) or anion species (W, Mo, P, or S). In the case of both Na and W, decreasing binding energy led to an increased $r_{\text{wet}}/r_{\text{dry}}$. The lower binding energy can be an indicator of lower bond strength, which is likely correlated to higher polarizability. However, this trend was not as clear with the other samples, likely due to the measurement being conducted ex situ. *In situ* Raman spectroscopy was also used to observe the W–O and Mo–O bonding at 800 °C (Fig. S20, ESI†), and similar spectra were observed between Na₂WO₄ and K₂WO₄, as well as Li₂MoO₄ and K₂MoO₄. Additional antistretching W–O modes were observed for Li₂WO₄ and Cs₂WO₄. This was also observed for Na₂MoO₄ and Cs₂MoO₄ and may be related to the low selectivity of these samples. However, structural changes that occur at 800 °C can be complicated and further work would be needed to fully understand these changes.

In conclusion, we have confirmed that alkali metal salts universally play a major role in the selective promotion of OCM through the addition of water for the OH radical mechanism. Although the alkali metal is an active site for OH radical formation through their peroxide form, the counter anion has a major influence on its activity and stability to form these unstable alkali peroxide intermediate, resulting in a stronger promotional effect of H₂O. Although different cations certainly influenced this effect, anions were found to play a more significant role in the formation of optimized surface active sites for OH radical formation. This work gives insight into why WO₄-based catalysts consistently show the highest performance for OCM reactions.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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