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# Methane Coupling Reaction in an Oxy-Steam Stream through an OH Radical Pathway by using Supported Alkali Metal Catalysts

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A universal reaction mechanism involved in the oxidative coupling of methane (OCM) is demonstrated under oxy-steam conditions using alkali-metal-based catalysts. Rigorous kinetic measurements indicated a reaction mechanism that is consistent with OH radical formation from a  $H_2O-O_2$  reaction followed by C–H activation in CH<sub>4</sub> with an OH radical. Thus, the presence of water enhances both the CH<sub>4</sub> conversion rate and the C<sub>2</sub> selectivity. This OH radical pathway that is selective for the OCM was observed for the catalyst without Mn, which sug-

## Introduction

The oxidative coupling of methane (OCM), the direct synthesis of  $C_2$  hydrocarbons from methane by using  $O_2$  and oxide catalysts at high temperatures, has been investigated for many years.<sup>[1]</sup> The simplified reaction pathway for the OCM that is commonly accepted in the literature is shown in Scheme 1. The sequential pathways to grow carbon chains account for the attainable yield of OCM processes because the products combust more rapidly than the CH<sub>4</sub> reactant.



**Scheme 1.** The simplified reaction pathway for the OCM at high conversion (dotted arrows: first order with respect to hydrocarbon concentration, solid arrows: second order with respect to hydrocarbon concentration).

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gests clearly that Mn is not the essential component in a selective OCM catalyst. The experiments with different catalyst compositions revealed that the OH'-mediated pathway proceeded in the presence of catalysts with different alkali metals (Na, K) and different oxo anions (W, Mo). This difference in catalytic activity for OH radical generation accounts for the different OCM selectivities. As a result, a high C<sub>2</sub> yield is achievable by using Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>, which catalyzes the OH'-mediated pathway selectively.

Until recently, the reaction was generally thought to be initiated by the formation of methyl radicals on the catalyst surfaces that then undergo gas-phase radical reactions (heterogeneous-homogeneous pathways).<sup>[2]</sup> The literature describes catalysts based on MgO or rare earth oxides for the OCM.<sup>[3]</sup> In addition, Mn alkali catalysts have been investigated.<sup>[4]</sup> Rigorous kinetic studies that use the state-of-the-art Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst for the OCM revealed that the addition of water to the reactant mixture can improve both the rate and selectivity.<sup>[5]</sup> Rather than CH<sub>4</sub> activation by the surface oxygen species (an O<sup>\*</sup>-mediated pathway), the OCM reaction was found to largely proceed through CH<sub>4</sub> activation by gas-phase OH radicals that are formed catalytically from the H<sub>2</sub>O–O<sub>2</sub> reaction (a OH<sup>\*</sup>-mediated pathway).<sup>[Sa]</sup>

This study addresses the site requirements for catalytic OH radical generation in an oxy-steam stream at high temperatures during an OCM reaction. Many OCM-active Mn-containing catalysts have been reported,<sup>[4]</sup> but whether these reducible Mn-originated sites are essential for water activation remains uncertain. We demonstrate that Na2WO4/SiO2 (without Mn species) yields a higher selectivity than its Mn-containing counterparts because the catalyst is not active for the less selective O\*-mediated pathway, which allows the OH radical pathway to predominate. These catalysts (without Mn) have been investigated previously,<sup>[6]</sup> but the effects of H<sub>2</sub>O were not considered. The melting points of  $Na_2WO_4$  (971 K) and Na<sub>2</sub>MoO<sub>4</sub> (960 K) are lower than the typical OCM operating temperatures (> 1000 K), which suggests that under OCM conditions, the catalyst surface is covered with these molten salts that can, for example, facilitate a phase transfer of the SiO<sub>2</sub> support from tridymite to cristobalite.<sup>[4d]</sup> Variation of the catalyst components demonstrates that a selective OH-mediated pathway within an OCM reaction depends on the catalyst for-

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mulation. We propose that alkali metals, not the reducible oxide, may be the active component for high selectivity. To the best of our knowledge, the experimentally obtained  $C_{2+}$  yields (> 27 %) are among the highest reported to date.

### **Results and Discussion**

### Kinetic analysis using Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> (low conversion)

We first focus on the initial steps of  $CH_4$  activation. The reaction pathway that dominates at low conversions for a selective catalyst, such as  $Na_2WO_4/SiO_2$ , is shown in Scheme 2. Zero



Scheme 2. The reaction pathway for the  $CH_4/O_2/H_2O$  reaction at low conversion.

conversion rates, determined by extrapolating the rates measured at various conversions to zero, were used to reflect the input conditions with the given reactant pressures.

The CH<sub>4</sub> conversion rate on a Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst (in the absence of H<sub>2</sub>O) is proportional to  $P_{CH_4}P_{O_2}^{1/2}$  (Figure 1 A and 1 B), which is consistent with the mechanism that involves the dissociative adsorption of O<sub>2</sub> that reacts with molecularly adsorbed CH<sub>4</sub>.<sup>[4e,5a]</sup> The elementary reaction steps involved in the surface O\*-mediated pathway for Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> are consistent with those reported for a Mn-containing catalyst, described as R1–R6 in Table 1.

To simplify the steps, the quasi-equilibrium steps for R1 and R2 are combined into R7. The rate for methane activation through this mechanism can be described as Equation (1) (Table 1), which is first order with respect to  $CH_4$  and half order with respect to  $O_2$  (Figure 1).

Table 1. Plausible elementary steps and rate equations for the surface O* pathway and gas-phase OH pathway.					
Reaction					
R1	$O_2 + * \underbrace{\overset{K'_{O_1}}{} O_2} *$				
R2	$O_2^* + * \underbrace{\kappa''_{O_2}}{2} 2O^*$				
R3	$CH_4 + * \overleftarrow{CH_4} CH_4 *$				
R4	$CH_4^* + O^* \xrightarrow{k_0 *} CH_3 + OH^* + *$				
R5	$2 \text{OH} \stackrel{\text{K-OH} *}{\longleftarrow} \text{O} \stackrel{\text{H}}{\rightarrow} \text{O}$				
R6	$H_2O^* \xrightarrow{K_{H_2O}*} H_2O$				
R7	$O_2 + 2^* \stackrel{K_{O_2}}{\longleftarrow} 2O^*$				
R8	$OH* \underbrace{K'_{OH+}}{} *+ OH' \text{ or } H_2O* + O* \underbrace{K'_{OH+}}{} *+ OH* + OH'$				
R9	$O_2 + 2H_2O \stackrel{K_{\text{OH}}}{\longrightarrow} 4OH'$				
R10	CH₄+OH <sup>•<u>k</u>•o+CH₃<sup>•</sup>+H₂O</sup>				
Eq. (1)	$r' = k_{O*} K_{CH_4} K_{O_2}^{1/2} P_{CH_4} P_{O_2}^{1/2}$				
Eq. (2) <sup>[a]</sup>	$r_{C_2} = k_{C_2} P_{CH_3}^2$				
Eq. (3) <sup>[a]</sup>	$r_{\rm CO_x} = k_{\rm CO_x} P_{\rm CH_3} P_{\rm O_2}^{\beta}$				
Eq. (4)	$r'' = k_{\rm OH} K_{\rm OH} P_{\rm CH_4} P_{\rm O_2}^{1/4} P_{\rm H_2O}^{1/2}$				
Eq. (5)	$r_{CH_4} = r' + r'' = k' P_{CH_4} P_{O_2}^{1/2} + k'' P_{CH_4} P_{O_2}^{1/4} P_{H_2O}^{1/2}$				
$[\mathbf{a}] P_{CH_3} = \frac{\sqrt{\left(k_{CO_1} P_{O_2}^{\beta}\right)^2 + 4k_{C_3} r_{CH_4} - k_{CO_1} P_{O_2}^{\beta}}}{2k_{C_2}}$					

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**Figure 1.** A) CH<sub>4</sub> partial pressure dependence and B) O<sub>2</sub> partial pressure dependence of the CH<sub>4</sub> conversion rates obtained by extrapolating the measured rates to zero (zero conversion rates) and C) C<sub>2</sub> selectivity (C<sub>2</sub>H<sub>6</sub>+C<sub>2</sub>H<sub>4</sub>) as a function of the CH<sub>4</sub> conversion (under various conditions without a H<sub>2</sub>O co-feed with a Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst; 0.1 g cat, 1073 K, 6–48 kPa CH<sub>4</sub>, 1–12 kPa O<sub>2</sub>, total pressure = 101 kPa balanced by He).

After the kinetically relevant C–H bond activation step of CH<sub>4</sub>, the methyl radicals can either react with another methyl radical or with an oxygen species (Scheme 2, Eqs. (2) and (3) in Table 1). The presence of  $O_2$  is essential to activate CH<sub>4</sub> (either through O\* or OH'), which leads to a nonzero selectivity for

 $CO_x$  at zero  $CH_4$  conversion. A high  $O_2$  pressure results in a low  $C_2$  selectivity at low  $CH_4$  conversions as indicated in Figure 1 C. In a previous study,<sup>[5b]</sup> the oxygen dependence  $\beta$  was associated with first-order CO formation (molecular  $O_2$  in the gas phase) and half-order  $CO_2$  formation (dissociated  $O_2$  on the surface (O\*)). We emphasize that, in any case, the catalysts should prevent the direct formation of  $CO_x$ .

Next, the CH<sub>4</sub> conversion rates were measured by using a Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst at constant CH<sub>4</sub> and O<sub>2</sub> pressures with varied H<sub>2</sub>O pressure. The rates as a function of the residence time at various H<sub>2</sub>O pressures are presented in Figure 2A. The CH<sub>4</sub> conversion rates improved drastically as the H<sub>2</sub>O pressure increased. Although the reason for the slight decrease in rates with increasing residence time in the presence of H<sub>2</sub>O remains unclear, the beneficial effects of H<sub>2</sub>O pressure on CH<sub>4</sub> conver-



**Figure 2.** Effect of water pressure on A) the CH<sub>4</sub> conversion rates as a function of the residence time, B) C<sub>2</sub> selectivity (C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>) as a function of the CH<sub>4</sub> conversion, C) and D) incremental CH<sub>4</sub> conversion rate (obtained from the measured differences between the rates with and without H<sub>2</sub>O) as a function of  $P_{D_2}^{1/4}P_{H_2}^{1/2}$  with a Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst (0.1 g, 1073 K, 10.0 kPa CH<sub>4</sub>, 1.7 kPa O<sub>2</sub>, 0–2.3 kPa H<sub>2</sub>O, total pressure = 101 kPa balanced by He).

sion rates are apparent (Figure 2A). The C<sub>2</sub> selectivity (C<sub>2</sub>H<sub>6</sub>+C<sub>2</sub>H<sub>4</sub>) during the same experiments is presented in Figure 2B. The selectivity also improved with increasing H<sub>2</sub>O pressures (at a given conversion). At these low conversion levels, the selectivity exceeded 90% at zero conversion, and mostly for C<sub>2</sub>H<sub>6</sub> formation with other products in smaller quantities (Figure 2C). This suggests that the direct combustion of CH<sub>4</sub> to CO<sub>x</sub> is minimized on the catalyst. C<sub>2</sub>H<sub>4</sub> is likely formed by the dehydrogenation of C<sub>2</sub>H<sub>6</sub> as it is extrapolated to zero selectivity can be explained by the accelerated CH<sub>3</sub><sup>•</sup> formation, which is followed by a second-order recombination of CH<sub>3</sub><sup>•</sup> to CO<sub>x</sub> with positive O<sub>2</sub> dependence [Eq. (3)]. This high sensitivity to O<sub>2</sub> pressure increases the rate of CO<sub>x</sub> formation over that of

 $C_2H_6$ , which results in the decreased  $C_2$  selectivity at higher  $O_2$  pressure (Figure 1 C). This high initial selectivity is also consistent with the observation that the catalyst lacks steam-reforming activity toward CO and  $H_2$ .<sup>[5b]</sup>

The rates at zero conversion were obtained similarly from the data acquired if various H<sub>2</sub>O pressures and CH<sub>4</sub>/O<sub>2</sub> mixtures were co-fed. The improved rates in the presence of H<sub>2</sub>O were associated with a positive kinetic order for H<sub>2</sub>O pressures. As indicated in the kinetic analysis (Figure 2D), the incremental rates between the H<sub>2</sub>O-present and H<sub>2</sub>O-absent rates were proportional to  $P_{O_2}^{1/4} P_{H_2O'}^{1/2}$  which is consistent with a reaction mechanism in which CH<sub>4</sub> is activated by guasi-equilibrated OH radicals from a H<sub>2</sub>O/O<sub>2</sub> mixture. The quasi-equilibrated nature of OH radical formation leads to R8 in Table 1.[5,7] Thus, the quasiequilibrated steps R5-R8 lead simply to R9. If an OH radical reacts with CH<sub>4</sub> in the gas phase, R10 occurs to generate a methyl radical. Notably, R10 is a pure homogeneous (gas-phase) reaction. The rate of this reaction can be described as Equation (4). The rate is proportional to  $P_{O_2}^{1/4}P_{H_2O_2}^{1/2}$ , which is consistent with Figure 2D. The rate expression for CH<sub>4</sub> activation (at least at low conversion) can be thus described based on two separate CH₄ conversion terms, the O\*-

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mediated and OH-mediated pathways as shown in Equation (5),<sup>[5a]</sup> in which  $k' = k_{O^{+}} K_{CH_4} K_{O_2}^{1/2}$  and  $k'' = k_{OH} K_{OH}$ .

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The measured apparent rate constants k' and k'', the rates for r' and r'', and their rate ratio r''/r' under typical oxy-steam conditions at 10 kPa CH<sub>4</sub>, 1.7 kPa O<sub>2</sub>, and 1.7 kPa H<sub>2</sub>O are summarized in Table 2. The ratio r''/r' provides a clear explanation of how the OH-mediated pathway dominates the O\*-mediated pathway. The r''/r' ratio can be strongly correlated with  $K_{OH'}$ /  $K'_{CH_4'}$  which is the ratio of the H<sub>2</sub>O and CH<sub>4</sub> adsorption coefficients. The presence of Mn in the catalyst clearly enhanced the rate constants for the CH<sub>4</sub> conversion with O\* (without H<sub>2</sub>O) to yield an apparent rate constant (k') for Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> (0.04 µmol g<sup>-1</sup> s<sup>-1</sup> kPa<sup>-3/2</sup>) that exceeds that for Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> (0.01 µmol g<sup>-1</sup> s<sup>-1</sup> kPa<sup>-3/2</sup>). Thus, Mn has been considered effective previously if a CH<sub>4</sub>/O<sub>2</sub> mixture (in the absence of H<sub>2</sub>O) was

introduced as a reactant.<sup>[4]</sup> The apparent rate constant for the OH<sup>-</sup>-mediated pathway (k'') was found be to  $0.12 \,\mu mol \, g^{-1} s^{-1} k Pa^{-7/4}$  for Mn/  $Na_2WO_4/SiO_2$  compared with  $0.21 \ \mu mol g^{-1} s^{-1} k Pa^{-7/4}$ for  $Na_2WO_4/SiO_2$ . Thus, r''/r' is 5.8 for the catalyst without Mn, which exceeds that for the catalyst with Mn (2.7) to result in predominant CH<sub>4</sub> activation through a OH-mediated pathway for Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>. The C<sub>2+</sub> selectivity on using Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> was notably higher than that with a Mncontaining catalyst for all CH<sub>4</sub> conversions, which is consistent with that predicted by ChemKin modeling in which a pure OHmediated pathway exhibits improved C<sub>2</sub> selectivity and yield.<sup>[5b]</sup>

The unique properties of  $Na_2WO_4/SiO_2$  for the generation of OH radicals from a H<sub>2</sub>O/O<sub>2</sub> mixture may arise from redox properties of the oxo anion (W). To investigate this, the CH<sub>4</sub> conversion rates were measured by using a Na<sub>2</sub>MoO<sub>4</sub>/SiO<sub>2</sub> catalyst at constant CH<sub>4</sub> and O<sub>2</sub> pressures with varied H<sub>2</sub>O pressure, and the results are shown in Figure 3. As with a Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst, the CH<sub>4</sub> conversion rates on using Na2MoO4/SiO2 increased with increasing H<sub>2</sub>O partial pressure (Figure 3A). The C<sub>2</sub> selectivity also improved drastically with increasing H<sub>2</sub>O pressures (at a given conversion; Figure 3B and 3C), but this selectiv**Table 2.** Rate constants for the surface O\* pathway and gas-phase OH pathway and the rates under typical conditions (0.1 g, 10 kPa  $CH_4$ , 1.7 kPa  $O_2$ , 1.7 kPa  $H_2O$ ).<sup>[a]</sup>

Catalyst	K	<i>k</i> "	ŕ	r″	r"/r′	
Mn/Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	0.040	0.21	1.16	3.64	2.7	
Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	0.011	0.12	0.32	2.15	5.8	
Na <sub>2</sub> MoO <sub>4</sub> /SiO <sub>2</sub>	0.016	0.058	0.46	1.00	1.9	
$Na_2WO_4/AI_2O_3$	0.027	0.016	0.78	0.80	0.9	
K <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	0.039	0.066	1.13	1.14	0.9	
Na <sub>2</sub> CO <sub>3</sub> /SiO <sub>2</sub>	n.d.	0.023	-	0.04	-	
[a] $r_{CH_4} = r' + r''$ , (surface O* pathway) $r' = k'P_{CH_4}P_{O_2}^{1/2}$ , (gas-phase OH pathway) $r'' = k''P_{CH_4}P_{O_2}^{1/2}P_{H_2O}^{1/2}$ . $r, r'$ and $r''$ in $\mu$ molg <sup>-1</sup> s <sup>-1</sup> , $kP_4$ in $\mu$ molg <sup>-1</sup> s <sup>-1</sup> , $k'$ in						



**Figure 3.** Effect of water pressure on A) the CH<sub>4</sub> conversion rates as a function of residence time, B) the C<sub>2</sub> selectivity (C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>) as a function of the CH<sub>4</sub> conversion, and C) incremental CH<sub>4</sub> conversion rate (obtained from the measured differences between the rates with and without H<sub>2</sub>O) as a function of  $P_{0_2}^{1/4}P_{H_2O}^{1/2}$  with a Na<sub>2</sub>MoO<sub>4</sub>/SiO<sub>2</sub> catalyst (0.1 g, 1073 K, 10.0 kPa CH<sub>4</sub>, 1.7 kPa O<sub>2</sub>, 0–2.3 kPa H<sub>2</sub>O, total pressure = 101 kPa balanced by He).

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ity was slightly lower than that for the Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst. Without H<sub>2</sub>O addition (CH<sub>4</sub>/O<sub>2</sub> mixture only), CO and CO<sub>2</sub> are formed significantly, and negligible C<sub>2</sub>H<sub>4</sub> selectivity at low conversion indicates that C<sub>2</sub>H<sub>4</sub> is the secondary product from C<sub>2</sub>H<sub>6</sub> dehydrogenation (Figure 3C). These incremental CH<sub>4</sub> conversion rates on using Na<sub>2</sub>MoO<sub>4</sub>/SiO<sub>2</sub> were correlated as a function of  $P_{O_2}^{1/4}P_{H_2O}^{1/2}$  (Figure 3D). The linear relationship of this plot is consistent with a mechanism that involves CH<sub>4</sub> activation through quasi-equilibrated OH<sup>-</sup>-mediated pathways. The r''/r'ratio is 1.9, which indicates that a OH<sup>-</sup>-mediated pathway is predominant under oxy-steam conditions, yet below that of Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>.

Further investigation was aimed to identify the active components of the OH radical pathways. The K<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>, Na<sub>2</sub>WO<sub>4</sub>/ Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub>/SiO<sub>2</sub> catalysts were investigated in a similar manner with particular attention paid to the effects of H<sub>2</sub>O. The beneficial effects of H<sub>2</sub>O on both the CH<sub>4</sub> conversion and C<sub>2</sub> selectivity were observed for all catalysts. The rate constants and the r''/r' ratios are compiled in Table 2. Large k' values and the resultant small r''/r' ratios for Na<sub>2</sub>WO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>WO<sub>4</sub>/ SiO<sub>2</sub> indicate that the surface O\*-mediated activation of CH<sub>4</sub> is relatively prominent on these catalysts. For improved C2 selectivity, the catalyst must be inert under CH<sub>4</sub> activation on the surface (Al<sub>2</sub>O<sub>3</sub> may not be because of its Lewis acidity), but sufficiently sensitive to generate OH radicals (K may be less sensitive than Na). Moreover, the absence of a W or Mo species (the experiments performed with a Na<sub>2</sub>CO<sub>3</sub> catalyst) also demonstrated exclusive activity for the OH-mediated pathway with no measurable rates confirmed for the surface O\*-mediated pathway. These data indicate that W or Mo is not essential for H<sub>2</sub>O activation with O<sub>2</sub>, but that alkali metal species (Na<sup>+</sup>, K<sup>+</sup>) are more likely (W or Mo stabilizes those alkali species). In the same experiment that uses quartz, no catalysis for CH<sub>4</sub> conversion was observed even in the presence of H<sub>2</sub>O (CH<sub>4</sub> is inert in both the presence and absence of water). The site requirement is also related to the active oxygen species involved in the activation of CH<sub>4</sub> and H<sub>2</sub>O, such as O<sup>\*</sup> or O<sub>s</sub> $-O^*$  etc., which are currently difficult to discern except that the kinetic analyses indicate the involvement of dissociated O2. The alkali metal species, which are often in the molten salt state at the reaction temperature, generally have a high affinity for H<sub>2</sub>O (to form hydroxides easily). These kinetic analyses demonstrate the universality and significance of the reaction mechanism involved in the OCM reaction that uses H<sub>2</sub>O as a co-reactant (i.e., the C-H bond activation by OH radicals formed catalytically).

#### **Catalyst characterization**

As described previously,  $Na_2WO_4$  and  $Na_2MOO_4$  are in a molten state under the reaction conditions because their melting points are below the reaction temperature ( $\geq$  1073 K; Table 3), which leads to a facile transfer of the crystal structure to a more rigid structure. The cristobalite phases dominate the samples, especially with the molten salts ( $Na_2WO_4$  and  $Na_2MOO_4$ ) and particularly after the OCM reactions (Figure 4). With the knowledge that alkali metals enhance the phase change, flux-assisted phase transformation is believed to occur **Table 3.** Salt melting points, BET surface areas, and C<sub>2</sub> selectivities  $(C_2H_6+C_2H_4)$  at 2% CH<sub>4</sub> conversion for the various catalysts (0.1 g, 1073 K, 10 kPa CH<sub>4</sub>, 1.7 kPa O<sub>2</sub>, total pressure = 101 kPa balanced by He).

Catalyst	Salt m.p. [K]	BET surface area [m²g <sup>-1</sup> ]	$C_2$ selectivity at 2% $CH_4$ conversion [%]	
$\label{eq:started} \begin{split} &Na_2WO_4/SiO_2\\ &Na_2MoO_4/SiO_2\\ &K_2WO_4/SiO_2\\ &Na_2WO_4/Al_2O_3 \end{split}$	971	1.9	88.0	
	960	1.7	45.0	
	1194	0.6	66.9	
	971	5.2	71.4	



Figure 4. XRD patterns of the  $K_2WO_4/SiO_2$ ,  $Na_2WO_4/SiO_2$ , and  $Na_2MoO_4/SiO_2$  catalysts before and after the reaction (AR).

at high temperatures. We do not consider this phase transfer to be critical to create a single active site for  $CH_4$  coupling (or OH radical generation); however, it aids in the inhibition of the combustion activity on the surface. The reaction contains  $H_2O$ as a sintering-facilitation reagent, and the typical reaction time per sample is longer than 2 days. The catalytic performance remains unchanged during the measurements.

# Dual-reactor experiments with $Na_2WO_4/SiO_2$ catalyst (high conversions)

A sequential dual-reactor system (Scheme 3) was used to achieve high conversions and yields by using Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>, the most selective catalyst investigated, with the introduction of additional  $O_2$  between the first and second reactors. The  $C_{2+}$ yields (all hydrocarbons except for the CH<sub>4</sub> reactant) measured at various reaction temperatures and pressures are shown in Figure 5. Some results of the CH<sub>4</sub> conversion, carbon selectivity, and C<sub>2</sub> and C<sub>2+</sub> yields under various conditions are summarized in Table 4. In a single reactor with a  $CH_4/O_2$  ratio of 3, the  $CH_4$ conversion reached ~37% with a  $C_2$  selectivity of ~64%. The  $C_{2+}$  yield thus exceeds 25% already with a single reactor. Further conversion of the  $\mathsf{CH}_4$  was attempted with the second reactor at various temperatures. The C<sub>2+</sub> yields improved only slightly, as confirmed by the experiments under various O2 pressures and reaction temperatures in the second reactor. The insensitivity of the O<sub>2</sub> pressure at high CH<sub>4</sub> conversion to the C<sub>2</sub> selectivity implies that all hydrocarbons have the same oxygen dependence to form CO<sub>x</sub>. Thus, the staged O<sub>2</sub> ap-



Scheme 3. Schematic image of the sequential dual-reactor system with O<sub>2</sub> addition.



**Figure 5.** C<sub>2+</sub> yield as a function of the CH<sub>4</sub> conversion using a sequential dual reactor for the CH<sub>4</sub>/O<sub>2</sub>/H<sub>2</sub>O reaction with a Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst (first reactor: 0.8 g, 1153 K, 10.0 kPa CH<sub>4</sub>, 0.8–3.3 kPa O<sub>2</sub>, 0–2.3 kPa H<sub>2</sub>O; second reactor: 0.4 g, 1073–1153 K, 0.8–2.4 kPa O<sub>2</sub> added to the stream from the first reactor, total pressure = 101 kPa balanced by He).

proach (the O<sub>2</sub> membrane reactor) is only useful at low CH<sub>4</sub> conversions as discussed previously (Scheme 2). Under such conditions, a sufficient C<sub>2</sub> concentration triggers the C<sub>2</sub> activation to form C<sub>3</sub> (and C<sub>4</sub>), which combust more rapidly (Scheme 1). The selectivity of C<sub>3</sub> or higher hydrocarbons (primarily C<sub>3</sub>H<sub>6</sub>) was ~3%. At 1123 K in the second reactor, the CH<sub>4</sub> conversion reached ~52% with a C<sub>2</sub>H<sub>4</sub> selectivity of ~40%. Overall, the C<sub>2+</sub> yield was 27.6%, which is higher than that reported over Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> (~26%),<sup>(5b)</sup> and among the high-

est hydrocarbon yields reported for simple oxygen-addition experiments.

Among the most unique properties of the  $Na_2WO_4/SiO_2$  catalyst is the high affinity of its surface for  $H_2O$  compared with hydrocarbons under steady-state conditions. As discussed in detail previously,<sup>[5b]</sup> the absence of strong hydrocarbon adsorption prevents the preferential combustion of a  $C_2H_4$  product (with

π electrons) on the surface. Moreover, the relative rates for the kinetically relevant C–H bond cleavage in each hydrocarbon through an OH radical pathway reflects only a Brønsted–Evans–Polanyi relationship, the C–H bond is stronger in C<sub>2</sub>H<sub>4</sub> (452 kJmol<sup>-1</sup>) than in CH<sub>4</sub> (439 kJmol<sup>-1</sup>), to yield a comparative-ly lower rate of C–H abstraction by the OH radical for C<sub>2</sub>H<sub>4</sub> than for CH<sub>4</sub> (1.2×10<sup>12</sup> or 1.6×10<sup>12</sup> cm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup>, respectively, at 1073 K), which results in an improved C<sub>2</sub> yield.<sup>[5b]</sup>

This study demonstrates the improved rates and yields of a methane coupling reaction under oxy-steam conditions. The kinetic analysis of the experiments that use a Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst is consistent with the quasi-equilibrated OH radical formation, which preferentially abstracts hydrogen from CH<sub>4</sub> over C<sub>2</sub>H<sub>4</sub>. The OCM reactions at high pressures remain a challenge because the carbon growth reactions are generally second order with respect to the hydrocarbon or relevant radical concentrations (Scheme 1).<sup>[3g]</sup> The formation of higher hydrocarbons, the concentrations of which increase with high CH<sub>4</sub> conversion, leads to reduced C<sub>2</sub> yields because of their high rates of oxidation to CO<sub>x</sub>.<sup>[3g, 5b]</sup>

### Conclusions

The presence of water in a  $CH_4/O_2$  mixture enhanced both the  $CH_4$  conversion rate and the  $C_2$  selectivity for the oxidative coupling of methane (OCM) that used alkali-metal-based catalysts. The reaction mechanism is consistent with OH radical formation from a  $H_2O-O_2$  reaction, followed by C–H activation in hydrocarbons with an OH radical. The contribution of this OH radical pathway that is selective for OCM over the surface O\* pathway predominantly accounts for the different OCM selec-

**Table 4.** Catalytic results from experiments that used a  $Na_2WO_4/SiO_2$  catalyst by using sequential dual reactors with  $O_2$  added between the first and second reactors (first reactor: 0.8 g, 1153 K, 10.0 kPa CH<sub>4</sub>, 3.3 kPa O<sub>2</sub>, 2.3 kPa H<sub>2</sub>O; second reactor: 0.4 g, 1073–1153 K, 2.4 kPa O<sub>2</sub> added to the stream from the first reactor, total pressure = 101 kPa balanced by He).<sup>[a]</sup>

	Conversion [%]		Selectivity [%]				Yield	eld [%]
	$CH_4$	$C_2H_4$	$C_2H_6$	C <sub>3</sub>	CO <sub>2</sub>	СО	C <sub>2</sub>	$C_{2+}$
1 <sup>st</sup> reactor (only) 1153 K	36.9	48.0	15.8	4.3	13.9	17.8	23.5	25.2
2 <sup>nd</sup> reactor 1153 K	53.1	37.2	9.2	2.9	23.8	26.4	24.6	26.4
2 <sup>nd</sup> reactor 1123 K	51.7	39.5	10.6	2.9	21.8	24.7	25.9	27.6
2 <sup>nd</sup> reactor 1073 K	44.7	43.2	13.5	3.4	18.2	21.2	25.3	27.0
[a] $H_2$ was detected with a	selectivity below 6% for hyd	rogen balance.						

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tivities. The OH-mediated pathway also proceeded with catalysts without Mn, W, or Mo, which suggests clearly that these components are not essential as an OH radical generator from a  $H_2O/O_2$  mixture. The universal mechanism for the selective OCM reaction is proposed to use the  $H_2O-O_2$  reaction on supported alkali metal catalysts.

### **Experimental Section**

For the catalyst preparation, SiO<sub>2</sub> (Sigma–Aldrich, Silica Gel, Davisil Grade 646, 35–60 mesh) or Al<sub>2</sub>O<sub>3</sub> (Evonik, Fumed Aluminum oxide Aeroxide Alu130) was used as a support to immobilize 5 wt% Na<sub>2</sub>WO<sub>4</sub>·2 H<sub>2</sub>O (Sigma–Aldrich, 99%), Na<sub>2</sub>MoO<sub>4</sub>·2 H<sub>2</sub>O (Sigma–Aldrich,  $\geq$  99.5%), K<sub>2</sub>WO<sub>4</sub> (Sigma–Aldrich, 94%), or Na<sub>2</sub>CO<sub>3</sub> (Fluka,  $\geq$  99.9999%) by wet impregnation. This sample was heated under a flow of dry air at 1173 K for 8 h at a rate of 2 Kmin<sup>-1</sup>.

The rates and selectivities of the  $CH_4/O_2/H_2O$  reactions were measured by using flow reactors using 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 by using a Honeywell controller coupled to a resistively heated furnace and measured with a K-type thermocouple set outside the catalyst bed. The  $CH_4$  (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 (278–293 K) was used to introduce the H<sub>2</sub>O gas.

The reactant and product concentrations were measured by using a VARIAN gas chromatograph 450GC with a programmed system that involved a molecular sieve 5 A column and a HayeSep Q column with a thermal conductivity detector, and a VARIAN CP-Wax 52 CB capillary column with a flame ionization detector. This configuration enables the differentiation of all C<sub>1</sub>–C<sub>4</sub> hydrocarbons. For H<sub>2</sub> detection, a micro-gas chromatograph (Agilent Technologies 3000A) equipped with thermally conductive molecular and plot U columns was used. Conversions, selectivities, and yields are reported on a carbon basis as cumulative integral values as follows [Eqs. (6)–(9)]:

Methane conv. [%] = 
$$\frac{\text{(total mols of carbon in products)}}{\text{(total mols of CH4 in)}} \times 100$$
(6)

or 
$$\frac{\text{(total mols of carbon in products)}}{\text{(total mols out including CH4)}} \times 100$$
 (7)

Select. [%] = 
$$\frac{(\text{mols of carbon in the specific product})}{(\text{total mols of carbon in products})} \times 100$$
 (8)

$$Yield [\%] = Methane \ conversion [\%] \times Selectivity [\%]/100$$
(9)

For rigorous kinetic analysis, linear regression was used to extrapolate the rates measured at various conversions to the rates at zero conversion. The obtained rates at zero conversion reflect the input conditions with the given reactant pressures strictly, which also minimizes the contribution of the heat generated by the reaction at low conversion levels. The XRD patterns of the products before and after the OCM reaction were obtained by using a Bruker DMAX 2500 X-ray diffractometer using CuK<sub> $\alpha$ </sub> radiation ( $\lambda$ =0.154 nm). The N<sub>2</sub> sorption studies were conducted by using a Micromeritics ASAP 2420 to determine the BET surface area. The results are compiled in the Supporting Information.

**Keywords:** alkali metals • kinetics • radicals • oxidative coupling • reaction mechanisms • supported catalysts

- a) J. S. Lee, S. T. Oyama, *Catal. Rev. Sci. Eng.* **1988**, *30*, 249–280; b) Z. Zhang, X. E. Verykios, M. Baerns, *Catal. Rev. Sci. Eng.* **1994**, *36*, 507–556; c) J. H. Lunsford, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 970–980; *Angew. Chem.* **1995**, *107*, 1059–1070; d) M. Yu. Sinev, Z. T. Fattakhova, V. I. Lomonosov, Yu. A. Gordienko, *J. Nat. Gas Chem.* **2009**, *18*, 273–287; e) U. Zavyalova, M. Holena, R. Schlögl, M. Baerns, *ChemCatChem* **2011**, *3*, 1935–1947.
- [2] K. Takanabe, J. Jpn. Pet. Inst. 2012, 55, 1-12.
- [3] a) G. E. Keller, M. M. Bhasin, J. Catal. 1982, 73, 9-19; b) T. Ito, J.-X. Wang, C.-H. Lin, J. H. Lunsford, J. Am. Chem. Soc. 1985, 107, 5062-5068; c) K. Otsuka, A. A. Said, K. Jinno, T. Komatsu, Chem. Lett. 1987, 77-80; d) K. Machida, M. Enyo, J. Chem. Soc. Chem. Commun. 1987, 1639-1640; e) J. A. Labinger, K. C. Ott, J. Phys. Chem. 1987, 91, 2682-2684; f) K. D. Campbell, J. H. Lunsford, J. Phys. Chem. 1988, 92, 5792-5796; g) J. A. Labinger, Catal. Lett. 1988, 1, 371-376; h) J. M. DeBoy, R. F. Hicks, J. Chem. Soc. Chem. Commun. 1988, 982-984; i) E. Morales, J. H. Lunsford, J. Catal. 1989, 118, 255-265; i) G. J. Hutchings, J. R. Woodhouse, M. S. Scurrell, J. Chem. Soc. Faraday Trans. 1 1989, 85, 2507-2523; k) J. A. Roos, S. J. Korf, R. H. J. Veehof, J. G. van Ommen, J. R. H. Ross, Appl. Catal. 1989, 52, 131-145; I) S. C. Reyes, E. Iglesia, C. P. Kelkar, Chem. Eng. Sci. 1993, 48, 2643-2661; m) S. C. Reyes, C. P. Kelkar, E. Iglesia, Catal. Lett. 1993, 19, 167-180; n) C. A. Mims, R. Mauti, A. M. Dean, K. D. Rose, J. Phys. Chem. 1994, 98, 13357-13372; o) S. Lacombe, H. Zanthoff, C. Mirodatos, J. Catal. 1995, 155, 106–116; p) P. M. Couwenberg, Q. Chen, G. B. Marin, Ind. Eng. Chem. Res. 1996, 35, 3999-4011; q) A. J. Colussi, V. T. Amorebieta, J. Catal. 1997, 169, 301-306; r) J. Coronas, J. Santamaría, Catal. Today 1999, 51, 377-389; s) Y. S. Su, J. Y. Ying, W. H. Green, J. Catal. 2003, 218, 321-333.
- [4] a) C. A. Jones, J. J. Leonard, J. A. Sofranko, J. Catal. 1987, 103, 311–319;
  b) X. Fang, S. Li, J. Lin, J. Gu, D. Yang, J. Mol. Catal. 1992, 6, 427; c) D. Wang, M. P. Rosynek, J. H. Lunsford, J. Catal. 1995, 155, 390–402; d) A. Palermo, J. P. H. Vazquez, A. F. Lee, M. S. Tikhov, R. M. Lambert, J. Catal. 1998, 177, 259–266; e) S. Pak, P. Qiu, J. H. Lunsford, J. Catal. 1998, 179, 222–230; f) S. Pak, J. H. Lunsford, Appl. Catal. A 1998, 168, 131–137; g) S. Ji, T. Xiao, S. Li, L. Chou, B. Zhang, C. Xu, R. Hou, A. P. E. York, M. L. H. Green, J. Catal. 2003, 220, 47–56; h) S. Hou, Y. Cao, W. Xiong, H. Liu, Y. Kou, Ind. Eng. Chem. Res. 2006, 45, 7077–7083; i) M. R. Lee, M.-J. Park, W. Jeon, J.-W. Choi, Y. W. Suh, D. J. Suh, Fuel Process. Technol. 2012, 96, 175–182.
- [5] a) K. Takanabe, E. Iglesia, Angew. Chem. Int. Ed. 2008, 47, 7689–7693;
   Angew. Chem. 2008, 120, 7803–7807; b) K. Takanabe, E. Iglesia, J. Phys. Chem. C 2009, 113, 10131–10145; c) V. Lomonosov, Yu. Gordienko, M. Sinev, Top. Catal. 2013, 56, 1858–1866.
- [6] A. Palermo, J. P. H. Vazquez, R. M. Lambert, Catal. Lett. 2000, 68, 191– 196.
- [7] a) L. C. Anderson, M. Xu, C. E. Mooney, M. P. Rosynek, J. H. Lunsford, J. Am. Chem. Soc. 1993, 115, 6322–6326; b) K. B. Hewett, L. C. Anderson, M. P. Rosynek, J. H. Lunsford, J. Am. Chem. Soc. 1996, 118, 6992–6997; c) K. B. Hewett, M. P. Rosynek, J. M. Lunsford, Catal. Lett. 1997, 45, 125–128.

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# **FULL PAPERS**

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## 

Methane Coupling Reaction in an Oxy-Steam Stream through an OH Radical Pathway by using Supported Alkali Metal Catalysts



**Make it methane:** A universal reaction mechanism involved in the oxidative coupling of methane is demonstrated under oxy-stream conditions by using alkali-metal-based catalysts. Rigorous kinetic measurements indicated a reaction mechanism that is consistent with OH radical formation from an  $H_2O-O_2$  reaction, followed by C–H activation in  $CH_4$ with an OH radical.