

# SITE REQUIREMENTS FOR SELECTIVE METHANE COUPLING REACTION IN AN OXY-STEAM STREAM

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## *Abstract*

Some catalysts enhance rates and selectivity for the oxidative coupling of methane (OCM) to generate C<sub>2</sub> hydrocarbon products in the presence of water. The kinetic measurements indicated a reaction mechanism that is consistent with the OH radical formation from an H<sub>2</sub>O-O<sub>2</sub> reaction, followed by C-H activation in CH<sub>4</sub> with an OH radical. This rather unrecognized reaction pathway with water is distinctive from the conventional mechanism proposed where CH<sub>4</sub> reacts with active surface oxygen species to generate methyl radicals in the gas phase. It is plausible that the surface active sites that lead to water activation might be different from the ones directly catalyzing CH<sub>4</sub>. Systematic investigation to vary the catalyst compositions revealed that the improvement of rates and selectivity in the presence of water was recognized when alkaline metals (Na, K) were present, consistent with their ability to activate water. On the other hand, some redox metals, such as Mn, W, Mo, were not essential components for realizing water activation pathway, but these components may play a role to stabilize and disperse alkali metals, utilizing a molten salt state prevalent during high temperature reaction. As a result, a high C<sub>2</sub> yield is achievable using Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> which selectively catalyzes the water pathway.

## *Keywords*

Oxidative coupling of methane, Alkali metal catalyst, Active site.

## **Introduction**

Lack of C<sub>2</sub> hydrocarbon yield from oxidative coupling of methane (OCM) essentially hinders its practical application [Labinger and Ott (1987), Labinger (1988), Takanabe (2012)]. A reaction mechanism involved in the OCM had been long described with oxygen species activated on the catalyst surface reacting with methane to generate methyl radicals in the gas phase [Campbell and Lunsford (1988)]. Recently, the rigorous kinetic measurements using a Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst found out that a reaction mechanism is consistent with the OH radical formation from an H<sub>2</sub>O-O<sub>2</sub> reaction [Anderson, L. C., et al. (1993). Hewett, K. B., et al. (1996), (1997).], followed by C-H activation in CH<sub>4</sub> with an OH radical [Takanabe and

Iglesia (2008), (2009)]. The presence of water enhances both the CH<sub>4</sub> conversion rate and the C<sub>2</sub> hydrocarbon selectivity, but what surface site is required to catalytically activate water still remains unclear. This study discusses the OCM results using various catalyst compositions, specifically focusing on the water effects on rates and selectivity.

## **Results and discussion**

The OCM kinetics at low conversions were analyzed at 1073 K with relatively low partial pressures (typically, 10 kPa CH<sub>4</sub>, CH<sub>4</sub>/O<sub>2</sub> = 3-12), so as to clearly observe the

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water effects [Liang et al. (2014)]. The addition of water had detrimental effects on Li/MgO and Sr/La<sub>2</sub>O<sub>3</sub>, well known OCM catalysts. The Li/MgO catalyst showed irreversible deactivation in the presence of water, coinciding with the significant loss of Li element from the catalyst during the reaction. The Sr/La<sub>2</sub>O<sub>3</sub> showed reversible rate decrease with increasing water pressure, consistent with competitive site blockage by the water derived adsorbed species. Some Na and K containing catalysts showed beneficial effects of water on both rates and selectivity to different degrees. The CH<sub>4</sub> conversion rates were expressed with the following Eq. (1), in which the first and second terms originate from the absence and presence of water, respectively:

$$r_{\text{CH}_4} = r_{\text{dry}} + r_{\text{wet}} = k'[\text{CH}_4][\text{O}_2]^{0.5} + k''[\text{CH}_4][\text{O}_2]^{0.25}[\text{H}_2\text{O}]^{0.5} \quad (1)$$

The results of  $k'$ ,  $k''$ ,  $r_{\text{wet}}/r_{\text{dry}}$  and C<sub>2</sub> selectivity for the kinetic analysis are compiled in Table 1. The  $r_{\text{wet}}/r_{\text{dry}}$  ratio reflects the significance of water contribution to the overall kinetics.

Table 1. Rate constants and rate ratios represented in the equation 1 using various catalysts under typical conditions

Catalyst	$k'$	$k''$	$r_{\text{wet}}/r_{\text{dry}}$	S [%]*
Mn/Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	0.040	0.21	3.2	90
Na <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	0.011	0.12	6.8	92
Na <sub>2</sub> MoO <sub>4</sub> /SiO <sub>2</sub>	0.016	0.058	2.2	72
K <sub>2</sub> WO <sub>4</sub> /SiO <sub>2</sub>	0.039	0.066	1.0	87
Na <sub>2</sub> CO <sub>3</sub> /SiO <sub>2</sub>	n.d.	0.002	-	87

[0.1 g, 1073 K, 10 kPa CH<sub>4</sub>, 1.7 kPa O<sub>2</sub>, 1.7 kPa H<sub>2</sub>O]

\* (C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>) selectivity at CH<sub>4</sub> conversion at 2%.

It can be seen that Mn is not the essential component to facilitate water activation ( $k''$ ), evident from higher  $r_{\text{wet}}/r_{\text{dry}}$  ratio for Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> than Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub>. The Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst, consistent with the previous report [Palermo, A. et al. (2000)], exhibits highly selective performance. The catalyst showed high stability for more than a week. The  $r_{\text{wet}}$  is prevalent on the catalysts with different oxo-anions (W, Mo), indicating that these oxo-anions and their redox properties are not essential as well. All the catalysts containing Na or K listed showed positive rate constant  $k''$ , indicative of their ability to activate water. Interestingly, the CH<sub>4</sub> conversion was detected only in the presence of water using Na<sub>2</sub>CO<sub>3</sub>/SiO<sub>2</sub> catalyst. It seems that the presence of alkali metals (Na, K) in the catalyst component is effective to activate water. These alkali metals are widely known to catalyze water activation in various catalytic applications, but for the OCM catalysts to be efficient, the component needs to be stable at high temperatures. Significant loss of Li from Li/MgO during OCM suggests that Li species likely sublimates, whereas Na and K seem to be more robust during the catalysis. It is worth mentioning that the melting points of Na<sub>2</sub>WO<sub>4</sub> and Na<sub>2</sub>MoO<sub>4</sub> were 971 and 960 K, respectively, indicating that these species likely exhibits molten state during OCM

reaction which was operated at 1073 K. This molten salt state would provide that the silica support, having cristobalite phase, is effectively covered from its exposure and disperse Na species effectively. This explains different rate constants for two terms appearing in Eq. (1), as evident from different  $r_{\text{wet}}/r_{\text{dry}}$  ratios obtained among the catalysts investigated.

It has been demonstrated that the presence of water introduces new reaction pathway for OCM. Using the Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst with introducing water in the reactant stream (0.8 g, 10 kPa CH<sub>4</sub>, 2.3 kPa H<sub>2</sub>O, CH<sub>4</sub>/O<sub>2</sub> = 3), the CH<sub>4</sub> conversion reached ~37% with a C<sub>2</sub> selectivity of ~64%. The ethylene, C<sub>2</sub> (C<sub>2</sub>H<sub>6</sub> + C<sub>2</sub>H<sub>4</sub>), and C<sub>2+</sub> (C<sub>2</sub> to C<sub>4</sub> hydrocarbons) yields were 17.7, 23.5 and 25.2% respectively, among the highest yields ever reported. Our microkinetic model enables to accurately predict the obtained product distribution and yields using the available gas-phase radical kinetics together with catalytic OH radical formation. Our results indicate that the selective OCM catalyst works as a selective OH radical generator.

## Conclusions

In the OCM literature, some controversy still remains in terms of attainable yields and identities of selective catalysts. The data demonstrated in this study provides some new insights of alkali-based catalysts operated at high temperature reaction on the mechanistic understanding of global OCM reaction network. Nevertheless, the reaction mechanism is still consistent that the attainable product yields are primarily limited by the more kinetically facile combustion of higher hydrocarbon, the formation of which cannot be avoided in the reaction mechanism led by this study.

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