

Critical impacts of interfacial water on C-H activation in photocatalytic methane conversion

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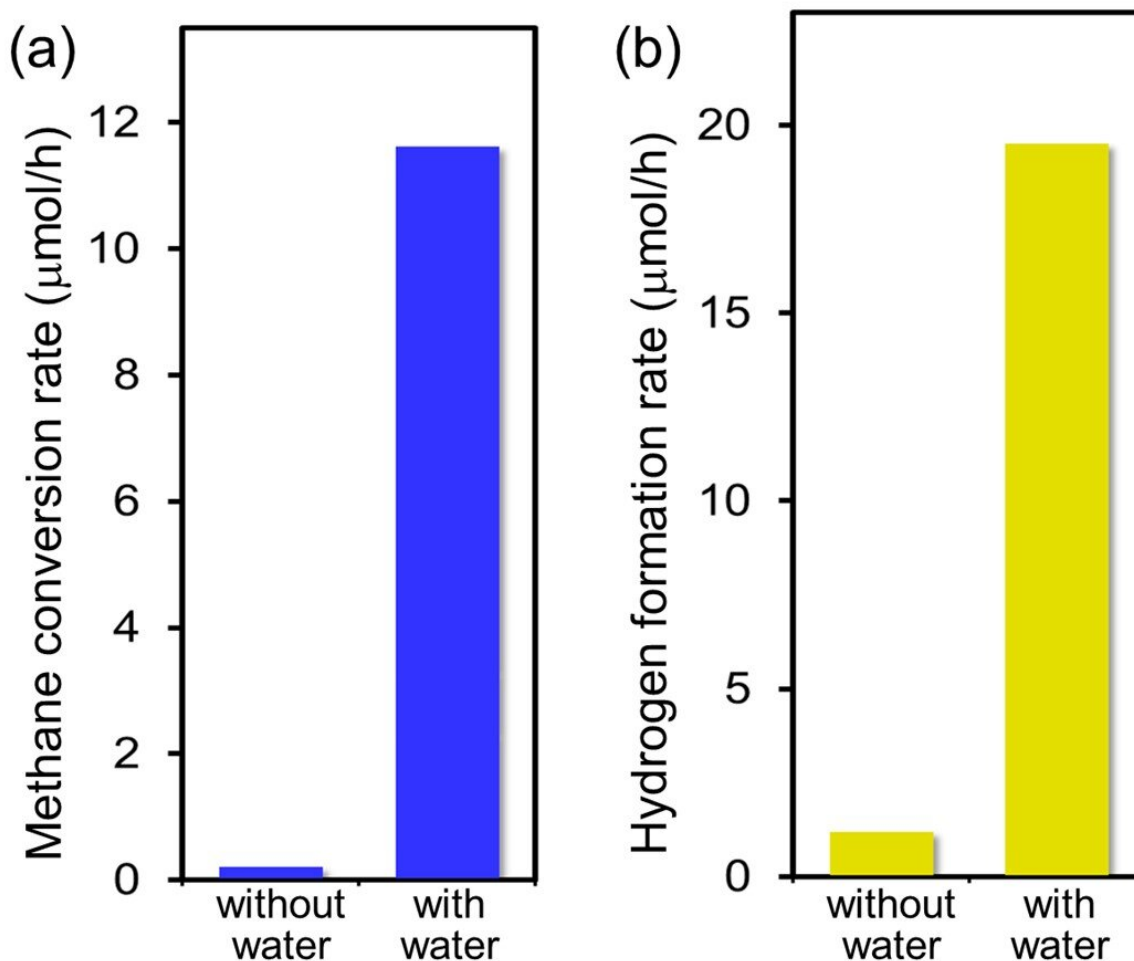


Fig. 1. (a) Methane conversion rates and (b) hydrogen formation rates on the Pt/Ga₂O₃ photocatalysts under ultraviolet irradiation at a methane partial pressure of 70 kPa and water partial pressures of 0 and 2 kPa at a sample

temperature of 318 K. The presence of interfacial water significantly enhances the photocatalytic activity at ambient temperatures and pressures. Credit: NINS/IMS

Non-thermal activation and utilization of methane, the main component of natural gas and a ubiquitous natural carbon resource, are among the global challenges for achieving sustainable society. However, incomplete knowledge on microscopic mechanisms of methane activation and hydrogen formation hampers the development of engineering strategies for the reaction system.

Very recently, in a study published in *Communications Chemistry*, researchers led by Toshiki Sugimoto, Associate Professor at the Institute for Molecular Science, succeeded in obtaining key molecular-level insights into the crucial role of interfacial water on the non-thermal C-H activation in photocatalytic [methane](#) conversion. Combining real-time mass spectrometry and [operando](#) infrared absorption spectroscopy with [ab initio molecular dynamics simulations](#), they showed that methane conversion is hardly induced by the [direct interaction](#) with the trapped hole at the surface O_{lat} site; instead, activation is significantly promoted by low barrier hydrogen abstraction from methane by photoactivated interfacial water species.

In water-mediated processes, the photocatalytic C-H activation is not the rate-determining step, which is in stark contrast to the case of traditional thermocatalytic methane reforming. Moreover, owing to the moderate stabilization of $\cdot\text{CH}_3$ in the hydrogen-bond network of water, overall photocatalytic conversion rates are dramatically improved by typically more than 30 times at [ambient temperatures](#) (~ 300 K) and pressures (~ 1 atm). As essentially opposed to thermal catalysis, methane photocatalysis no longer requires high-pressure methane gas (> 20 atm) in the presence

of adsorbed water layer.

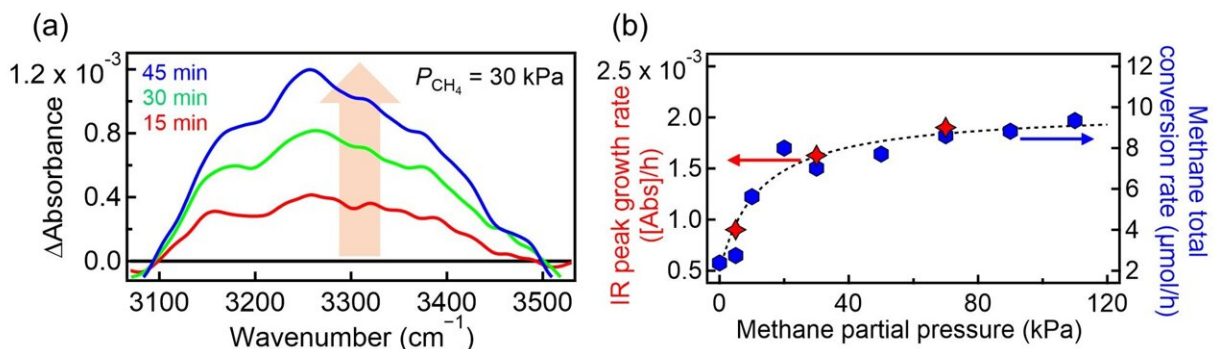


Fig. 2. (a) Time evolution of operando infrared (IR) spectra in the O–H stretching region for Pt/Ga₂O₃ photocatalysts under ultraviolet irradiation at a CH₄ pressure of 30 kPa and a D₂O pressure of 2 kPa. The O–H peak growth indicates the hydrogen abstraction on catalyst surfaces by photoactivated interfacial water species (CH₄(gas) + •OD(ad) → •CH₃(ad) + HDO(ad)). (b) Growth rate of the O–H peak (left axis) and CH₄ total conversion rate (right axis) on the Pt/Ga₂O₃ photocatalysts as functions of methane partial pressure; there is a good correlation between the two plots. Credit: NINS/IMS

Water-assisted effects are noticeable also in ethane formation, although water is not explicitly involved in the homocoupling reaction equation ($2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$). These results indicate that interfacial water kinetically plays crucial roles beyond the traditional thermodynamic concept of redox potential, in which oxidation of water by surface trapped holes is less thermodynamically favored than methane oxidation: $E^\circ_{\cdot\text{OH}/\text{H}_2\text{O}} = 2.73 \text{ V}$ and $E^\circ_{\cdot\text{CH}_3/\text{CH}_4} = 2.06 \text{ V}$ versus the standard hydrogen electrode.

Notably, these water-assisted effects are commonly observed for several representative photocatalysts with different band-gap energy, such as

TiO₂, Ga₂O₃, and NaTaO₃, indicating that the incorporation of methane into photoactivated interfacial hydrogen-bond network is essential key for the non-thermal activation of methane.

This work not only expands the molecular-level understanding of the non-thermal C-H activation and conversion, but also provides a fundamental basis for the rational interface design of non-thermal catalytic systems toward the effective and sustainable utilization of methane under ambient conditions.

More information: Critical impacts of interfacial water on C–H activation in photocatalytic methane conversion, *Communications Chemistry* (2023). [DOI: 10.1038/s42004-022-00803-3](https://doi.org/10.1038/s42004-022-00803-3)

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