Beyond reduction cocatalysts: A new paradigm for the role of metal cocatalysts in photocatalysis

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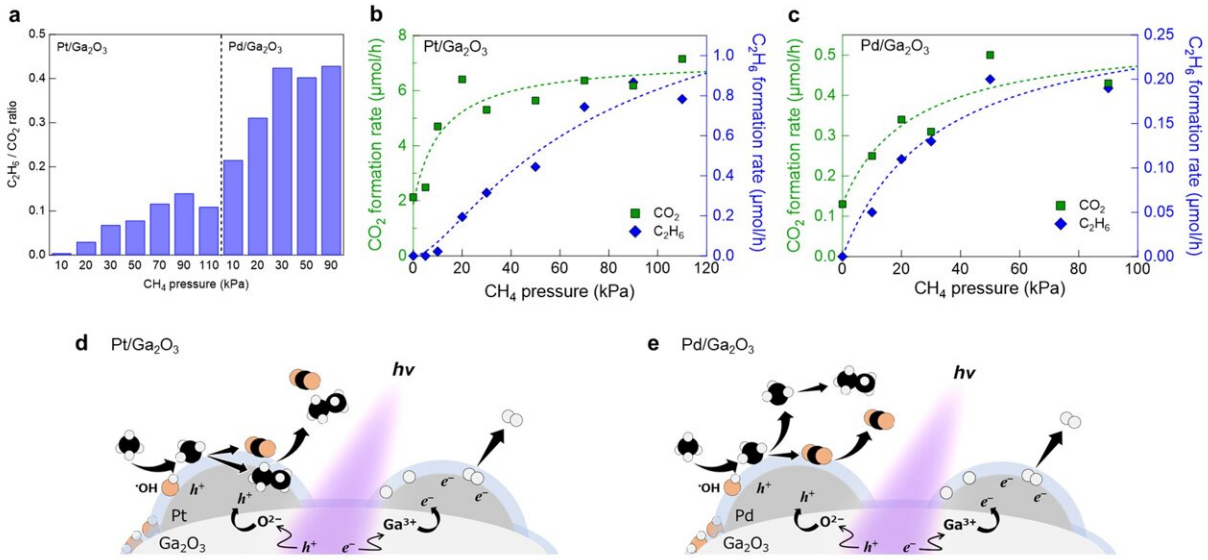


(a) The C_2H_6 to CO_2 ratios of Pt/Ga_2O_3 and Pd/Ga_2O_3 photocatalysts. The Pd cocatalyst promotes C_2H_6 formation more efficiently than the Pt cocatalyst. Methane pressure dependence on the formation rates of CO_2 and C_2H_6 over (b) Pt/Ga_2O_3 and (c) Pd/Ga_2O_3 photocatalysts at ~323 K. The pressure of water vapor was fixed at 2 kPa. Schematic illustration of photocatalytic methane oxidation and reduction taking place on (d) Pt and (e) Pd cocatalysts covered with a single water layer. Credit: Toshiki Sugimoto

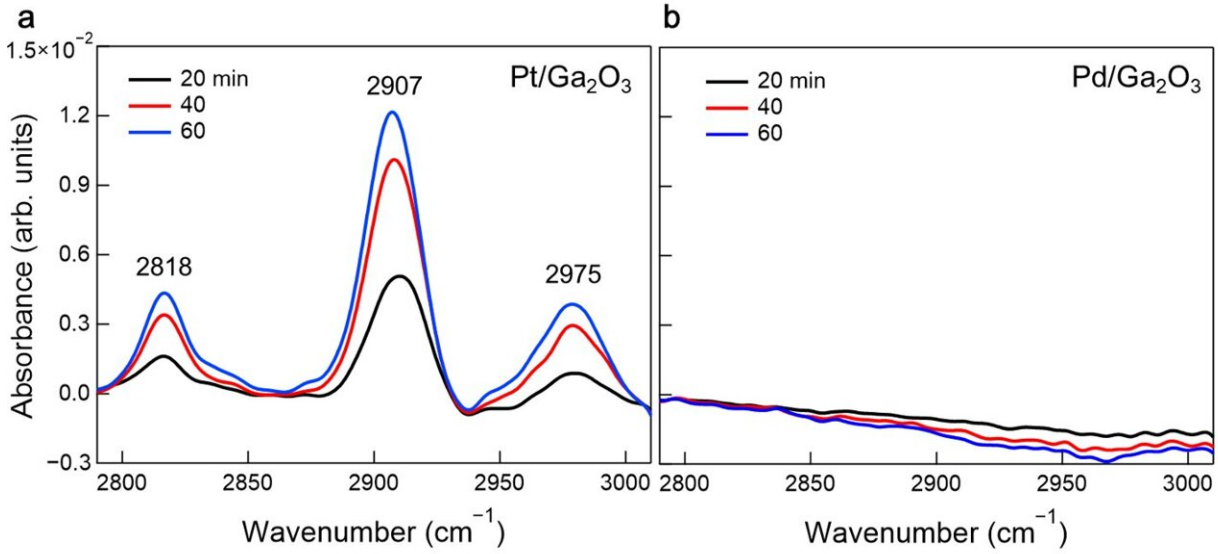
The photocatalytic conversion of methane with a ubiquitous and clean

oxidant of water has the potential to develop into an on-site and on-demand chemical technology for the green utilization of methane in an environmentally benign and sustainable way.

However, rational design of next-generation photocatalysts is hindered by the lack of molecular-level understanding of hole-driven oxidation kinetics, active sites, and resultant photocatalytic performance.

The research group led by Toshiki Sugimoto, Associate Professor at the Institute for Molecular Science, has demonstrated that metal cocatalysts loaded on a semiconductor photocatalyst play critical roles in modulating surface oxidation kinetics and resultant oxidation selectivity.

Real-time mass spectrometric analysis of gaseous products under systematically-controlled methane pressures revealed that the Pt-loaded Ga_2O_3 photocatalyst predominantly promoted the total oxidation of methane toward CO_2 on its surface, while the Pd-loaded photocatalyst exhibited a higher selectivity for C_2H_6 formation through the gas-phase coupling of free $\bullet CH_3$.



Time evolution of operando infrared spectra in the C–H stretching region for (a) Pt/Ga_2O_3 and (b) Pd/Ga_2O_3 photocatalysts under ultraviolet light irradiation at methane and water pressure of 30 and 2 kPa, respectively. The appearance of the C–H peaks on Pt/Ga_2O_3 demonstrates methane oxidation taking place on its surface. No C–H peaks on Pd/Ga_2O_3 indicates the low population of the hydrocarbon intermediates due to the desorption of the methyl radical intermediate. Credit: Toshiki Sugimoto

This difference in methane oxidation kinetics was corroborated by operando infrared absorption spectroscopy that observed surface intermediates under working conditions. Moreover, the research group demonstrated that the Pt cocatalyst itself was oxidized by photogenerated holes.

These experimental results demonstrated the critical roles of metal cocatalysts as a reservoir of photogenerated holes and an effective reaction site for methane oxidation processes. Generally, metal cocatalysts have been recognized for half a century as reduction cocatalysts that exclusively accumulate photogenerated electrons and promote reduction reactions such as H_2 evolution.

Based on this conventional assumption, hole-accumulated metal cocatalysts are assumed to act as charge recombination centers and inhibit photocatalysis. In contrast, this research group verified that both H_2 evolution and methane oxidation were accelerated by metal cocatalyst loading. These experimental results indicate that photogenerated electrons and holes are separately trapped at different metal cocatalyst particles while avoiding charge recombination and promoting redox reactions.

Thus, the systematic operando investigation of the photocatalytic

oxidation of methane (i.e., the most inert and simplest organic compound) and water (i.e., one of the key molecules in photocatalysis) provides a new paradigm for the role of metal cocatalysts in photocatalysis and thus contributes to developing a cocatalyst-based surface engineering strategy for controlling non-thermal oxidation reactions.

The paper is published in the journal *Angewandte Chemie International Edition*.

More information: Hikaru Saito et al, Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water**, *Angewandte Chemie International Edition* (2023). DOI: 10.1002/anie.202306058