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# Critical impacts of metal cocatalysts on oxidation kinetics and optimal reaction conditions of photocatalytic methane reforming†

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**Metal cocatalysts in photocatalysis are typically regarded as promoting only the reduction reactions. Here, we demonstrate that photocatalytic oxidation kinetics and optimal pressure of methane vary significantly with the loading amount of metal cocatalysts. These variations are well described by kinetic analyses treating molecular-level congestion of oxidation intermediates.**

Photocatalysis represents a promising approach for driving redox reactions using light, surpassing thermodynamic limitations.<sup>1–6</sup> Most advanced photocatalyst systems rely on noble metal cocatalysts to achieve high photocatalytic activity.<sup>7,8</sup> Indeed, numerous studies have demonstrated that the incorporation of metal cocatalysts significantly improves the activity of semiconductor-based photocatalysts.<sup>9,10</sup> Conventionally, it has been widely accepted that the metal cocatalysts act mostly as sinks of photogenerated electrons ( $e^-$ ) and serve exclusively as reduction sites.<sup>7,8</sup>

Some previous studies offered new insights into the role of metal cocatalysts in photocatalysis. For instance, previous density functional theory calculations<sup>11</sup> and infrared spectroscopy<sup>12</sup> have suggested that holes ( $h^+$ ) generated through band-gap excitation of semiconductor photocatalysts can be trapped by metal cocatalysts. This hypothesis is based on the simple assumption that  $h^+$ -accumulating metal cocatalysts act as recombination centers for photogenerated  $e^-$  and  $h^+$ , without investigating the actual photocatalytic performance. By contrast, our recent study combining *operando* spectroscopy with real-time mass spectrometry demonstrated that  $e^-$  and  $h^+$  can be separately captured by different metal cocatalysts, and the metal cocatalysts play key roles not only in promoting reduction reactions but also in accelerating oxidation reactions, while minimizing charge recombination.<sup>13</sup> Furthermore, metal cocatalysts not only enhance overall photocatalytic activity but also influence the oxidation

selectivity.<sup>13</sup> These recent findings highlight the need for a deeper understanding of the microscopic roles of metal cocatalysts, beyond the conventional view that they merely promote reduction reactions by accumulating only photogenerated  $e^-$ .<sup>7,8</sup>

In this study, we provide further experimental evidence that metal cocatalysts directly impact the photocatalytic oxidation processes. The oxidation process is recognized as the rate-determining step of photocatalysis,<sup>14–16</sup> and the oxidation kinetics should be affected by modulation of this step. To examine whether variations in metal cocatalysts alter the dynamics and kinetics of the rate-determining oxidation step, we investigated the effects of loading amounts of metal cocatalysts on photocatalytic methane conversion with water. Methane is the main component of natural gas and a ubiquitous natural resource. Due to its robust C–H bonds, achieving methane conversion under ambient temperatures and pressures poses a significant challenge in advancing sustainable technologies.<sup>17</sup> Conventional thermocatalytic methane conversion requires harsh conditions ( $>1000$  K and  $>20$  atm),<sup>18</sup> in contrast, photocatalysis offers a more sustainable approach by enabling methane activation and oxidation under ambient conditions ( $\sim 300$  K and  $\sim 1$  atm).<sup>17</sup> Herein, we focused on the Pt- or Pd-loaded gallium oxide ( $\text{Ga}_2\text{O}_3$ ) particles as robust model systems for photocatalytic methane reforming.<sup>13,15,19</sup> Through controlled experiments under varying methane pressures ( $P_{\text{CH}_4}$ ), we observed that the amount of metal cocatalysts significantly influences the  $P_{\text{CH}_4}$  dependence of the photocatalytic performance, resulting in pronounced modulation of the optimal  $P_{\text{CH}_4}$  conditions below ambient pressures. This variation suggests that the loading of metal cocatalysts affects the congestion of intermediate species involved in methane oxidation processes. These results highlight the crucial role of metal cocatalysts as active sites also for the oxidation reaction.

$\beta\text{-Ga}_2\text{O}_3$  is a well-known  $d^{10}$  photocatalyst<sup>2</sup> with stable activity and robustness.<sup>20</sup> The four  $\beta\text{-Ga}_2\text{O}_3$  samples containing either 0.01 wt% or 1 wt% of metal Pt or Pd cocatalysts ( $\text{Pt}(0.01 \text{ wt\%})/\text{Ga}_2\text{O}_3$ ,  $\text{Pd}(0.01 \text{ wt\%})/\text{Ga}_2\text{O}_3$ ,  $\text{Pt}(1 \text{ wt\%})/\text{Ga}_2\text{O}_3$ ,  $\text{Pd}(1 \text{ wt\%})/\text{Ga}_2\text{O}_3$ ) were prepared by the impregnation method (see Note S1-1, ESI,<sup>†</sup> for details). As described in detail in Note S1-2 (ESI<sup>†</sup>), the photocatalytic performance of these metal-loaded  $\text{Ga}_2\text{O}_3$  samples was evaluated by irradiating a deep

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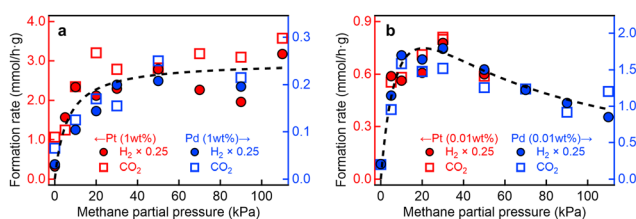
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ultraviolet (UV) lamp ( $\sim 90 \text{ mW cm}^{-2}$  at  $260 \pm 15 \text{ nm}$ ) at various  $P_{\text{CH}_4}$  under a fixed water vapor pressure ( $P_{\text{H}_2\text{O}}$ ) of 2 kPa. Notably, the photocatalytic activity under LED light irradiation at 390 nm was low, although loading the Pt and Pd cocatalysts enhanced the light absorption in this wavelength region (Fig. S1-5, ESI†).<sup>13</sup> This indicates that  $e^-$  and  $h^+$  species generated by the excitation of the metal cocatalysts<sup>21</sup> have little contribution, whereas those generated by the band-gap excitation of  $\text{Ga}_2\text{O}_3$  dominantly induce photocatalytic methane conversion.<sup>13</sup> Under the irradiation of a deep UV lamp, the sample temperature was  $\sim 318 \text{ K}$  and a single layer of adsorbed water molecules covered the sample surfaces at  $P_{\text{H}_2\text{O}} = 2 \text{ kPa}$  ( $\sim 20\%$  relative humidity for 318 K samples)<sup>22-24</sup> as described in Note S1-3 (ESI†).

Fig. 1 illustrates the  $P_{\text{CH}_4}$  dependence of the formation rates of  $\text{H}_2$  ( $R_{\text{H}_2}$ ) and  $\text{CO}_2$  ( $R_{\text{CO}_2}$ ) for the four photocatalyst samples. The rate of  $\text{H}_2$  evolution was approximately four times higher than that of  $\text{CO}_2$  formation ( $R_{\text{CO}_2} \approx 0.25 R_{\text{H}_2}$ ), indicating nearly stoichiometric  $\text{CO}_2$  production in the steam methane reforming reaction ( $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ ). In addition,  $\text{C}_2\text{H}_6$  derived from the side reaction ( $2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$ )<sup>25</sup> was also detected, as will be discussed later (Fig. 3).

As reported previously for the Pt(1 wt%)/ $\text{Ga}_2\text{O}_3$  and Pd(1 wt%)/ $\text{Ga}_2\text{O}_3$  photocatalysts,<sup>13,15</sup>  $R_{\text{H}_2}$  and  $R_{\text{CO}_2}$  showed a strong dependence on  $P_{\text{CH}_4}$ ; the rates increased sharply with  $P_{\text{CH}_4}$  below  $\sim 30 \text{ kPa}$  (0.3 atm) and nearly reached saturation value at  $\sim 100 \text{ kPa}$  (1 atm). In contrast, we found that the  $P_{\text{CH}_4}$  profiles for the Pt(0.01 wt%)/ $\text{Ga}_2\text{O}_3$  and Pd(0.01 wt%)/ $\text{Ga}_2\text{O}_3$  photocatalysts differ markedly from those for the 1 wt% metal-loaded samples (Fig. 1b); while  $R_{\text{H}_2}$  and  $R_{\text{CO}_2}$  increased with  $P_{\text{CH}_4}$  below  $\sim 20 \text{ kPa}$ , they began to decline at  $P_{\text{CH}_4}$  above  $\sim 20 \text{ kPa}$ . Thus, for the 1 wt% metal-loaded samples, the photocatalytic performance for methane conversion is almost maximized at ambient pressure ( $\sim 1 \text{ atm}$ ), whereas the optimal  $P_{\text{CH}_4}$  is around 20 kPa, well below 1 atm, for the 0.01 wt% metal-loaded samples. The observed variation in the  $P_{\text{CH}_4}$  profile (Fig. 1) indicates that the microscopic redox reaction kinetics of photocatalytic steam methane reforming is affected by the loading amount of metal cocatalysts. Beyond the conventional assumption that the role of metal cocatalysts is limited solely to reduction reactions in the semiconductor bandgap photoexcitation scheme,<sup>7,8</sup> our experimental results clearly show the impact of metal cocatalysts not only on reduction ( $\text{H}_2$  evolution) but also on oxidation ( $\text{CO}_2$  formation) processes in this widely used photoexcitation scheme.



**Fig. 1**  $P_{\text{CH}_4}$  profiles of photocatalytic steam methane reforming. Formation rates of  $\text{H}_2$  and  $\text{CO}_2$  for (a) Pt(1 wt%)/and Pd(1 wt%)/ $\text{Ga}_2\text{O}_3$  photocatalysts, and (b) Pt(0.01 wt%)/and Pd(0.01 wt%)/ $\text{Ga}_2\text{O}_3$  photocatalysts under UV irradiation as a function of  $P_{\text{CH}_4}$  at  $P_{\text{H}_2\text{O}} = 2 \text{ kPa}$ . Curve fitting results based on eqn (3) with  $U = 40 \text{ kJ mol}^{-1}$  and eqn (4) with  $U = 37 \text{ kJ mol}^{-1}$  are also shown in (a) and (b), respectively.

To provide microscopic insights on the influence of metal cocatalyst loadings on the reaction kinetics, detailed analysis was carried out on the observed  $P_{\text{CH}_4}$  dependence of the photocatalytic performance (Fig. 1). In general, the  $\text{CH}_4$  oxidation process toward  $\text{CO}_2$  can be divided into three steps (Fig. 2a and b):<sup>13,15</sup> (i) dissociative adsorption and desorption of  $\text{CH}_4$  at vacant active sites, (ii) sequential reactions involving surface intermediate species,<sup>26</sup> and (iii) desorption of the final products, primarily  $\text{CO}_2$  (see also Note S2, ESI†). The C–H cleavage of  $\text{CH}_4$  in the first step is initiated by hydrogen abstraction from photoactivated interfacial water species,<sup>15</sup> resulting in the formation of activated methane species ( $X_1 = \bullet\text{CH}_3$ ) that subsequently chemisorb onto the catalyst surfaces (Fig. 2a and b). This process leads to the  $P_{\text{CH}_4}$  dependence of the coverage of  $\bullet\text{CH}_3$  ( $\theta_{\text{CH}_3}$ ) similar to the Langmuir adsorption isotherm as follows:<sup>13,15</sup>

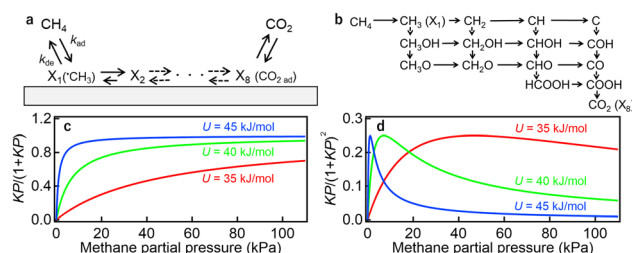
$$\theta_{\text{CH}_3} = KP_{\text{CH}_4}/(1 + KP_{\text{CH}_4}), \quad (1)$$

where  $K$  is the equilibrium constant for the first step (dissociative adsorption of methane and desorption of methyl radical;  $\text{CH}_4(\text{gas}) + \bullet\text{OH}(\text{ad}) \leftrightarrow \bullet\text{CH}_3(\text{ad}) + \text{H}_2\text{O}(\text{ad})$ ), expressed as  $K \equiv k_{\text{ad}}/k_{\text{de}} \propto \exp(U/k_{\text{B}}T_{\text{s}})$ . Here,  $k_{\text{B}}$  and  $T_{\text{s}}$  represent the Boltzmann constant and surface temperature, respectively, and  $U$  denotes the stabilization energy of the  $\bullet\text{CH}_3(\text{ad})$  intermediate (see Note S2-1 for details of the kinetic analysis, ESI†).

Notably, the product yields linearly increased with irradiation time,<sup>13,15</sup> indicating that the reactions proceeded under steady-state conditions. In the case where the reaction of adsorbed  $\bullet\text{CH}_3$  is rate-determining,<sup>13,15</sup>  $R_{\text{CO}_2}$  under steady-state conditions is dominated by the reaction of  $\bullet\text{CH}_3$  as follows:

$$R_{\text{CO}_2} \approx k'_1 \theta_{\text{CH}_3} \theta_v, \quad (2)$$

where  $k'_1$  is the rate constant factor for the rate-determining reaction process, and  $\theta_v \equiv 1 - \sum \theta_{X_i}$  ( $\theta_{X_i}$  is the coverage of the  $i$ -th intermediate species ( $i = 1, 2, \dots, 8$ , see Fig. 2a and b) that block the reaction sites) represents the fraction of vacant surface sites available for the forward reaction of  $\bullet\text{CH}_3$  species toward  $\text{CO}_2$  (see also Note S2 for details, ESI†). When the density of surface reaction sites is high enough that few active sites are occupied ( $\theta_v \approx 1$ ) in steady reaction



**Fig. 2** Reaction scheme and kinetic analysis of photocatalytic steam methane reforming. (a) Surface reaction pathway for the conversion of  $\text{CH}_4$  to  $\text{CO}_2$ , where  $X_i$  ( $i = 1, 2, \dots, 8$ ) represents reaction intermediates; specifically,  $X_1$  and  $X_8$  denote methyl radical ( $\bullet\text{CH}_3$ ) and adsorbed  $\text{CO}_2$ , respectively. For simplicity, the contribution of OH radical species ( $\bullet\text{OH}$ ) generated via water oxidation ( $\text{H}_2\text{O} + h^+ \rightarrow \bullet\text{OH} + h^+$ )<sup>15</sup> is omitted in the diagram. (b) Possible reaction intermediate species from  $\text{CH}_4$  to  $\text{CO}_2$  in Fig. 2a through hydrogen abstraction or hydroxylation by photoactivated water species.<sup>26</sup> (c) and (d)  $P_{\text{CH}_4}$  dependence of  $R_{\text{CO}_2}$  given by (c) eqn (3) and (d) eqn (4) at different values of  $U$  (35, 40, and  $45 \text{ kJ mol}^{-1}$ ).

conditions, eqn (2) is approximated as

$$R_{\text{CO}_2} \approx k'_1 \theta_{\text{CH}_3} = k'_1 (KP_{\text{CH}_4} / (1 + KP_{\text{CH}_4})). \quad (3)$$

The  $P_{\text{CH}_4}$  profiles of  $R_{\text{CO}_2}$  at typical values of  $U$  are displayed in Fig. 2c. As  $U$  increases, the reaction activity tends to start increasing at the lower  $P_{\text{CH}_4}$ . Then, with increasing  $P_{\text{CH}_4}$ , reaction activity monotonically increases as an upward convex curve and then saturates in response to the abundance of the rate-determining intermediate species.

In contrast, when the density of active sites is not sufficiently high, the coverage of intermediate species competitively affects the fraction of vacant surface sites. Since the majority of the surface intermediates are  $\bullet\text{CH}_3$  ( $\sum \theta_{\text{X}_i} \approx \theta_{\text{CH}_3}$ ) in the case where the reaction of adsorbed  $\bullet\text{CH}_3$  intermediates is rate-determining,<sup>13,15</sup> the fraction of vacant sites is approximated as  $\theta_v \approx 1 - \theta_{\text{CH}_3}$ , yielding the following form of eqn (2):

$$R_{\text{CO}_2} \approx k'_1 \theta_{\text{CH}_3} (1 - \theta_{\text{CH}_3}) = k'_1 (KP_{\text{CH}_4} / (1 + KP_{\text{CH}_4}))^2. \quad (4)$$

In this case, although the reaction activity starts to increase at the lower  $P_{\text{CH}_4}$  region, it begins to decrease with increasing  $P_{\text{CH}_4}$  after reaching a maximum value (Fig. 2d). This characteristic  $P_{\text{CH}_4}$  profile arises from a balance between two competing effects (Fig. S2-3, ESI†): the positive impact of increasing the abundance of the rate-determining intermediate species and the negative impact of molecular-level congestion due to the reduced availability of vacant active sites for further reactions of the rate-determining intermediate species ( $\text{X}_1 \rightarrow \text{X}_2$  in Fig. 2a and b). It should also be noted that, even if the rate-determining step is not the forward reaction of  $\bullet\text{CH}_3$  ( $\text{X}_1$ ) but rather another surface reaction involving different intermediate species ( $\text{X}_i \rightarrow \text{X}_{i+1}$  in Fig. 2a and b), the  $P_{\text{CH}_4}$  dependencies similar to eqn (3) and (4) are derived as discussed in Note S3 (ESI†).

For the Pt(1 wt%)/Ga<sub>2</sub>O<sub>3</sub> and Pd(1 wt%)/Ga<sub>2</sub>O<sub>3</sub> photocatalysts,  $P_{\text{CH}_4}$  profiles of  $R_{\text{CO}_2}$  were well-fitted to eqn (3) with a stabilization energy  $U$  of 40 kJ mol<sup>-1</sup> (Fig. 1a), as reported in our previous studies.<sup>13,15</sup> On the other hand, the reaction activity for the Pt(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> and Pd(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> photocatalysts behaved differently, showing a better fit to eqn (4) compared to eqn (3) with a similar  $U$  value of 37 kJ mol<sup>-1</sup> (Fig. 1b). These curve-fitting analyses indicate that a sufficient number of active sites are provided for the 1 wt% loading of metal cocatalysts, avoiding competitive occupation of active sites by intermediate species. In contrast, the 0.01 wt% loading provides a limited number of active sites for intermediate species, resulting in the competition of positive and negative effects of active site occupation by intermediate species. Therefore, the observed modulation of reaction kinetics upon loading amount of metal cocatalysts provides compelling evidence that the metal cocatalysts themselves function as reaction fields for the photocatalytic oxidation.<sup>13</sup> These results further suggest that the photogenerated e<sup>-</sup> and h<sup>+</sup> migrate separately from Ga<sub>2</sub>O<sub>3</sub> to the metal cocatalyst particles,<sup>13</sup> enabling certain metal cocatalysts to act as reduction sites by capturing electrons, while others function as oxidation sites by trapping holes, as discussed in detail in Note S4 (ESI†).

Additional important evidence supporting that metal cocatalysts are deeply involved in molecular-level dynamics and congestion of photocatalytic oxidation processes has been obtained. This is demonstrated by focusing on the simultaneously induced side-reaction of methane into ethane ( $2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$ ). Fig. 3 illustrates the  $P_{\text{CH}_4}$  dependence of ethane formation rates ( $R_{\text{C}_2\text{H}_6}$ ) for the four photocatalyst samples. In contrast to  $R_{\text{CO}_2}$  (Fig. 1), the  $P_{\text{CH}_4}$  profiles of  $R_{\text{C}_2\text{H}_6}$  not only vary depending on the loading amount of metal cocatalysts but also vary depending on the metal element of cocatalysts (Fig. 3). As detailed in our previous study,<sup>13</sup> the  $P_{\text{CH}_4}$  profiles for the Pt(1 wt%)/Ga<sub>2</sub>O<sub>3</sub> and Pd(1 wt%)/Ga<sub>2</sub>O<sub>3</sub> photocatalysts (Fig. 3a) were described by the second-order and first-order reactions of the surface adsorbed  $\bullet\text{CH}_3$  intermediate species, respectively, as follows:

$$R_{\text{C}_2\text{H}_6}(\text{Pt 1 wt}\%) \approx k''_1 \theta_{\text{CH}_3}^2 = k''_1 \left( (KP_{\text{CH}_4})^2 / (1 + KP_{\text{CH}_4})^2 \right), \quad (5)$$

$$R_{\text{C}_2\text{H}_6}(\text{Pd 1 wt}\%) \approx k''_1 \theta_{\text{CH}_3} = k''_1 (KP_{\text{CH}_4} / (1 + KP_{\text{CH}_4})), \quad (6)$$

where  $k''_1$  is a rate constant. The apparent difference of the reaction order indicates that the coupling of  $\bullet\text{CH}_3$  intermediates ( $2\bullet\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ ) occurs on the catalyst surfaces (eqn (5) and Fig. S5-1a, S5-2, ESI†) for the Pt(1 wt%)/Ga<sub>2</sub>O<sub>3</sub>, while it proceeds in the gas phase for the Pd(1 wt%)/Ga<sub>2</sub>O<sub>3</sub> (eqn (6) and Fig. S5-1b, S5-5, ESI†).<sup>13</sup>

As the main reaction ( $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ ), we found that the limited 0.01 wt% loading of metal cocatalysts also has a significant impact on the  $P_{\text{CH}_4}$  profiles of  $R_{\text{C}_2\text{H}_6}$  (Fig. 3b). For the Pt(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> photocatalyst,  $R_{\text{C}_2\text{H}_6}$  steeply declined at  $P_{\text{CH}_4} > 10$  kPa after the initial increase at  $P_{\text{CH}_4} < 10$  kPa. A similar trend was observed for the Pd(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> photocatalyst, although the decline was more gradual compared to the Pt(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> photocatalyst. These non-monotonic  $P_{\text{CH}_4}$  profiles are derived from the competition between the positive impact of increasing the abundance of the rate-determining  $\bullet\text{CH}_3$  intermediate species and the negative impact of their molecular-level congestion due to the reduced availability of vacant active sites for further reactions. Then, these observed  $P_{\text{CH}_4}$  profiles were well-fitted with the following equations explicitly incorporating the effect of competing occupation

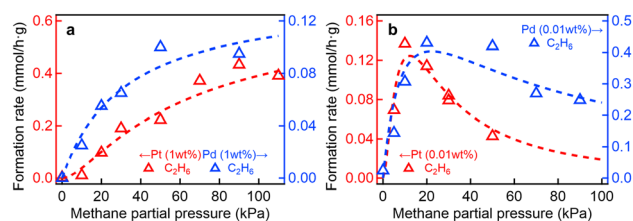


Fig. 3  $P_{\text{CH}_4}$  profiles of photocatalytic ethane formation from methane. Formation rates of  $\text{C}_2\text{H}_6$  for (a) Pt(1 wt%)/and Pd(1 wt%)/Ga<sub>2</sub>O<sub>3</sub> photocatalysts, and (b) Pt(0.01 wt%)/and Pd(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> photocatalysts under UV irradiation at  $P_{\text{H}_2\text{O}} = 2$  kPa. Curve fitting results based on eqn (5) and (6) with  $U = 36$  kJ mol<sup>-1</sup>, eqn (7) with  $U = 39$  kJ mol<sup>-1</sup>, and eqn (8) with  $U = 37$  kJ mol<sup>-1</sup> are also shown in (a) and (b).





of limited active sites by intermediate species ( $\theta_v \approx 1 - \theta_{CH_3}$ ).

$$\begin{aligned} R_{C_2H_6}(\text{Pt } 0.01 \text{ wt}\%) &\approx k_1''(\theta_{CH_3}\theta_v)^2 \\ &= k_1''(\theta_{CH_3}(1 - \theta_{CH_3}))^2 \\ &= k_1''\left((KP_{CH_4})^2 / (1 + KP_{CH_4})^4\right), \end{aligned} \quad (7)$$

$$\begin{aligned} R_{C_2H_6}(\text{Pd } 0.01 \text{ wt}\%) &\approx k_1''(\theta_{CH_3}\theta_v) \\ &= k_1''\theta_{CH_3}(1 - \theta_{CH_3}) \\ &= k_1''(KP_{CH_4} / (1 + KP_{CH_4})^2). \end{aligned} \quad (8)$$

The decline of  $R_{C_2H_6}$  is more significant for eqn (7) than eqn (8) (Fig. S5-7b, ESI†). As described in detail in Note S5 (ESI†), the apparent difference of the reaction order for  $\theta_{CH_3}\theta_v$  indicates that the homocoupling of methyl radical intermediates ( $2^\bullet\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ ) occurs on the catalyst surfaces (eqn (7) and Fig. S5-1a, S5-3, ESI†) for the Pt(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> sample, while it proceeds in the gas phase for the Pd(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> sample (eqn (8) and Fig. S5-1b, S5-6, ESI†).<sup>13</sup> Even though the homocoupling of  $^\bullet\text{CH}_3$  proceeds in the gas phase for the Pd(0.01 wt%)/Ga<sub>2</sub>O<sub>3</sub> sample (Fig. S5-1b, ESI†), manifestation of the negative  $P_{CH_4}$  impact in the apparent first order reaction suggests that the desorption of  $^\bullet\text{CH}_3$  into the gas phase occurs after it migrates from its initial adsorption site to a nearby vacant site that is more preferable for desorption (see Fig. S5-4, ESI† for more precise picture). Note that, in the situation where the competitive occupation of active sites by intermediate species is negligible ( $\theta_v \approx 1$ ), eqn (7) and (8) correspond to eqn (5) and (6), respectively. Thus, our results clearly demonstrate that the competitive occupation of active surface sites by reaction intermediates and the resulting modulation of reaction kinetics emerges also in the side reaction pathway of methane partial oxidation ( $\text{CH}_4 \rightarrow ^\bullet\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ ). Owing to this effect, the optimal  $P_{CH_4}$  condition for the photocatalytic ethane formation also significantly varied with the amount of metal loading (Fig. 3a and b). Therefore, the observed modulation of ethane formation kinetics also provides compelling evidence that the metal cocatalysts themselves functions as active sites for oxidative photoactivation. Furthermore, the homocoupling pathway for ethane formation is independent of the loading amount of metal cocatalysts (1 wt% or 0.01 wt%) but varies with the elements of metal cocatalysts used (Pt or Pd). This is also a manifestation of the phenomena that the metal cocatalysts fundamentally influence oxidation kinetics and dynamics.

Finally, we emphasize that our concept of metal cocatalysts also provides a rationale for previously reported, yet incomprehensible, results in photocatalytic oxidation. For instance, variations in the activity of photocatalytic oxidation have been reported for semiconductor photocatalysts loaded with metal cocatalysts of different elements and/or loading amount.<sup>27–29</sup> Nevertheless, metal cocatalysts have traditionally been regarded solely as the trapping site of  $e^-$  and the resultant promoters of reduction reactions.<sup>7,8</sup> This interpretation arises from the seemingly plausible assumption that more efficient oxidation reactions are simply driven by an increased number of  $h^+$  that avoid annihilative charge recombination with  $e^-$  due to the preferential trapping/consumption of  $e^-$  facilitated by metal cocatalysts.<sup>11,12</sup> Beyond this classical picture, our results provide a series of solid evidence that the metal

cocatalyst actively takes part in photocatalytic oxidation and modulates oxidation kinetics/dynamics, shedding new light on the complex interplay between cocatalyst loading and interfacial reaction.

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## Data availability

The data and analytical details supporting this article have been included as part of the ESI†

## Conflicts of interest

There are no conflicts to declare.

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