

Article

# Oxidative Dehydrogenation of Methane When Using TiO<sub>2</sub>- or WO<sub>3</sub>-Doped Sm<sub>2</sub>O<sub>3</sub> in the Presence of Active Oxygen Excited with UV-LED

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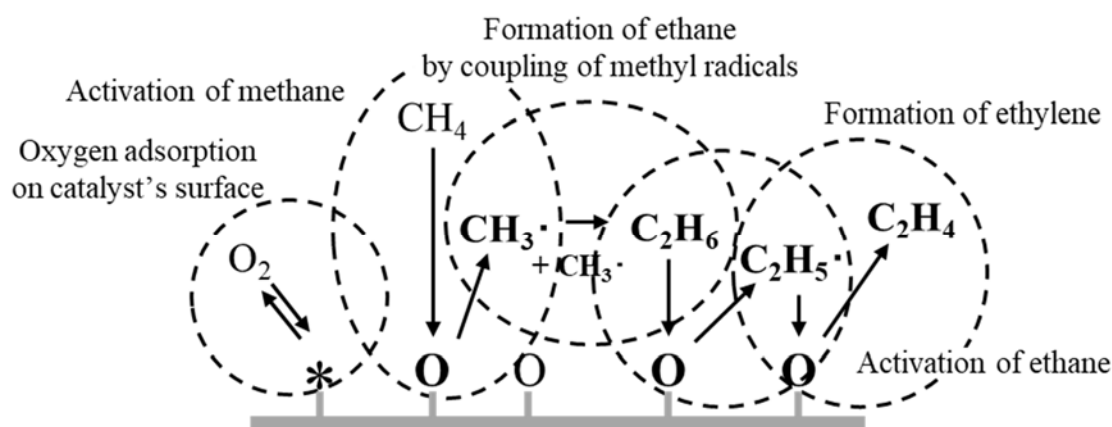
**Abstract:** There are active oxygen species that contribute to oxidative coupling or the partial oxidation during the oxidative dehydrogenation of methane when using solid oxide catalysts, and those species have not been definitively identified. In the present study, we clarify which of the active oxygen species affect the oxidative dehydrogenation of methane by employing photo-catalysts such as TiO<sub>2</sub> or WO<sub>3</sub>, which generate active oxygen from UV-LED irradiation conditions under an oxygen flow. These photo-catalysts were studied in combination with Sm<sub>2</sub>O<sub>3</sub>, which is a methane oxidation coupling catalyst. For this purpose, we constructed a reaction system that could directly irradiate UV-LED to a solid catalyst via a normal fixed-bed continuous-flow reactor operated at atmospheric pressure. Binary catalysts prepared from TiO<sub>2</sub> or WO<sub>3</sub> were either supported on or kneaded with Sm<sub>2</sub>O<sub>3</sub> in the present study. UV-LED irradiation clearly improved the partial oxidation from methane to CO and/or slightly improved the oxidative coupling route from methane to ethylene when binary catalysts consisting of Sm<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are used, while negligible UV-LED effects were detected when using Sm<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub>. These results indicate that with UV-LED irradiation the active oxygen of O<sub>2</sub><sup>-</sup> from TiO<sub>2</sub> certainly contributes to the activation of methane during the oxidative dehydrogenation of methane when using Sm<sub>2</sub>O<sub>3</sub>, while the active oxygen of H<sub>2</sub>O<sub>2</sub> from WO<sub>3</sub> under the same conditions afforded only negligible effects on the activation of methane.

**Keywords:** methane; oxidative dehydrogenation; active oxygen; UV-LED; TiO<sub>2</sub>; WO<sub>3</sub>; Sm<sub>2</sub>O<sub>3</sub>

## 1. Introduction

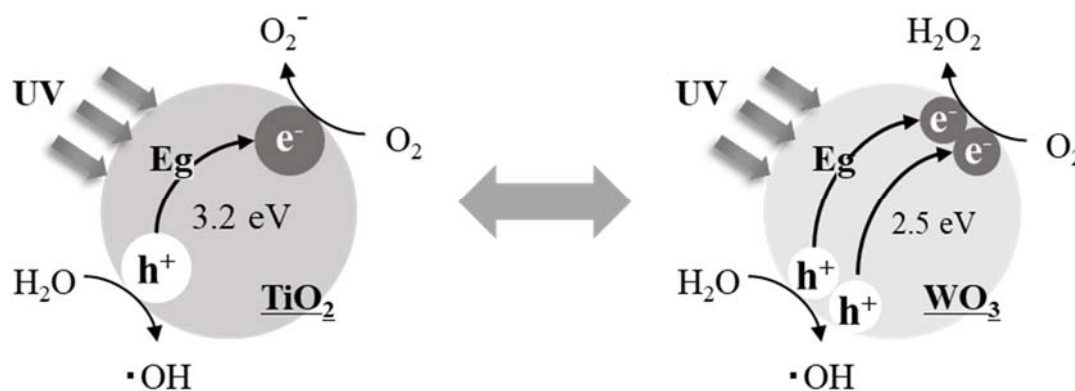
The conversion of methane to high value-added chemicals is an important issue in the field of catalyst research. In recent years, research on the catalytic reaction of methane has been actively conducted due to progress in the production technology of natural gas, which consists mainly of methane gas [1–3]. Although methane has the potential for conversion to a variety of important chemicals, its application as a raw material in catalytic reactions has been limited due to chemical stability. Therefore, methane is still used mainly as fuel.

To overcome the stability problem, many researchers are studying the direct conversion of methane to value-added chemicals such as methanol [4], carbon monoxide [5], ethylene [6], and aromatic compounds [7]. The direct conversion of methane is considered the most efficient way to use methane gas because the desired product requires only a one-step catalytic reaction. In particular, the oxidative coupling of methane (OCM) to ethylene and ethane has been the subject of much research over the past three decades since these C<sub>2</sub> hydrocarbons are the most widely used petrochemicals in the world. In the OCM reaction, methane reacts with oxygen exothermically on a solid oxide catalyst to produce these C<sub>2</sub> hydrocarbons together with water [8]. It is generally accepted that gaseous oxygen and active oxygen derived from a solid oxide catalyst could contribute to the oxidative conversion of methane [9–11]. Furthermore, the OCM is believed to consist of both heterogeneous and homogeneous reactions. First, in a heterogeneous reaction, active oxygen in the catalyst extracts hydrogen from methane to generate methyl radicals. The methyl radicals are then dimerized to C<sub>2</sub> hydrocarbons by a homogeneous gas-phase reaction (Scheme 1) [12–15]. Contributions have been proposed from active oxygen species such as O<sub>2</sub><sup>-</sup>, OH, H<sub>2</sub>O<sub>2</sub>, or <sup>1</sup>O<sub>2</sub> (singlet oxygen) together with gas-phase oxygen (O<sub>2</sub>) or catalytic lattice oxygen (O<sup>2-</sup>), but exactly what kind of active oxygen species contribute to the oxidative dehydrogenation of methane is yet to be clarified [16–21].



Scheme 1. Mechanism for the oxidative coupling of methane.

In the present study, we focused on the characteristics of photo-catalysts. Photo-catalysts such as titanium oxide (TiO<sub>2</sub>) and tungsten oxide (WO<sub>3</sub>) activate oxygen when electrons (e<sup>-</sup>) are excited by irradiation from an excitation light (UV-LED in the present study) and holes (h<sup>+</sup>) are sequentially generated, which results in the formation of active oxygen (Scheme 2).



Scheme 2. Production of active oxygen species via UV irradiation of TiO<sub>2</sub> and WO<sub>3</sub>.

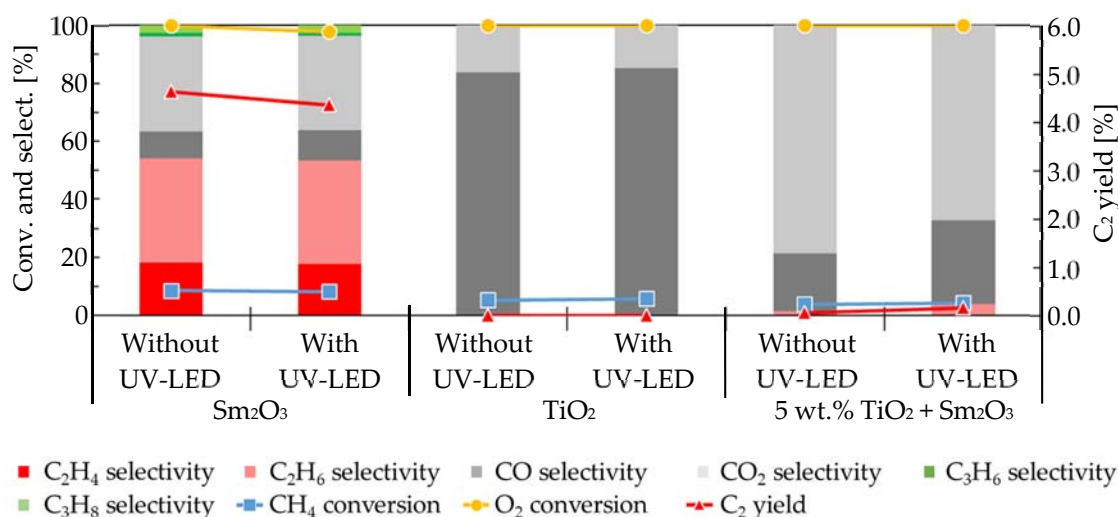
Based on Scheme 2, the oxidative dehydrogenation of methane was studied via contact with samarium oxide (Sm<sub>2</sub>O<sub>3</sub>; OCM-catalyst) and by examining the active oxygen species generated via

irradiating UV-LED irradiation of either  $\text{TiO}_2$  or  $\text{WO}_3$  (photo-catalyst) under a gaseous  $\text{O}_2$  atmosphere. It is generally accepted that  $\text{O}_2^-$  is generated from a one-electron reduction of  $\text{TiO}_2$ , and  $\text{H}_2\text{O}_2$  is generated from a two-electron reduction of  $\text{WO}_3$  [22]. When the active oxygen species derived from either  $\text{TiO}_2$  or  $\text{WO}_3$  contacted  $\text{Sm}_2\text{O}_3$  during the oxidative dehydrogenation of methane, the product distribution was expected to depend on the presence or absence of UV-LED irradiation. The purpose of this study was to confirm and clarify the contributions of each of the active oxygen species. It is noteworthy that titanium and tungsten have been used as the active species in various catalysts for the oxidative coupling of methane [23,24].

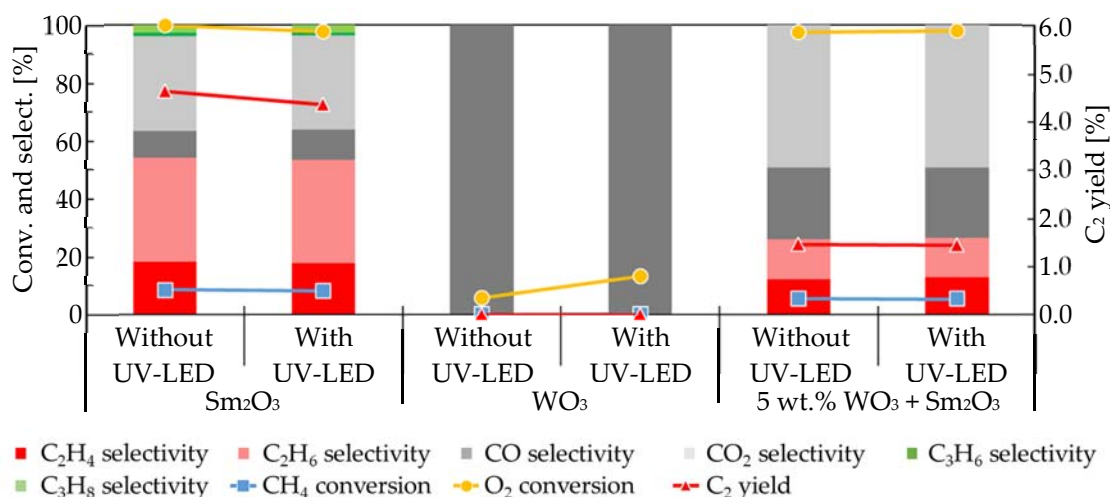
## 2. Results and Discussion

This study involved both mixed- and supported-catalysts that consisted of  $\text{Sm}_2\text{O}_3$  together with  $\text{TiO}_2$  or  $\text{WO}_3$ . Based on our preliminary experiments, the loading of photo-catalysts such as  $\text{TiO}_2$  and  $\text{WO}_3$  was fixed at 5 wt.%. First, the mixed-catalyst activity using 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$  was tested together with that of either  $\text{Sm}_2\text{O}_3$  or  $\text{TiO}_2$ . The specific surface areas of  $\text{Sm}_2\text{O}_3$ ,  $\text{TiO}_2$ , and 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$  were 7, 47, and 22  $\text{m}^2/\text{g}$ , respectively. Figure 1 shows the effect that UV-LED irradiation exerted on the oxidative dehydrogenation of methane at  $T = 898 \text{ K}$ ;  $P(\text{CH}_4) = 28.7 \text{ kPa}$ ; and  $P(\text{O}_2) = 2.03 \text{ kPa}$  ( $P(\text{CH}_4)/P(\text{O}_2) = 14.2$ ). Since stable catalytic activity was detected on all catalysts used to the point of 4.5 h on-stream, the activity at 0.75 h on-stream was discussed in the present study. As shown in Figure 1, UV-LED irradiation of  $\text{Sm}_2\text{O}_3$  showed no advantageous effects on either  $\text{C}_2$  yield or on the conversions of  $\text{O}_2$  and  $\text{CH}_4$ , while CO selectivity was slightly changed from 9.4% to 10.5% by the irradiation. A similar effect of UV-LED on  $\text{TiO}_2$  yielded CO selectivity of 83.8% to 85.2%. It should be noted that the conversions of  $\text{CH}_4$  and  $\text{O}_2$  were not influenced by the irradiation of UV-LED due to the oxygen-limiting conditions. When adding 5 wt.%  $\text{TiO}_2$  into  $\text{Sm}_2\text{O}_3$  (5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$ ), the unique nature of  $\text{Sm}_2\text{O}_3$  that allows coupling with methane was mostly masked by the nature of  $\text{TiO}_2$  that allows the partial oxidation of methane, and this resulted in a slight formation of  $\text{C}_2\text{H}_6$  on 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$ . Furthermore, an evident improvement in CO selectivity of from 19.9% to 28.9% was detected followed by a suppression of  $\text{CO}_2$  selectivity of from 78.6% to 67.2% after UV-LED irradiation of the mixed-catalyst. It should be noted that  $\text{C}_2\text{H}_6$  selectivity was also slightly improved from 1.5% to 3.9% via UV-LED irradiation using 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$ . Therefore,  $\text{O}_2^-$  generated via the UV-LED irradiation of  $\text{TiO}_2$  under a gaseous  $\text{O}_2$  atmosphere seemed to contribute to the acceleration of the partial oxidation of  $\text{CH}_4$  to CO together with the oxidative dehydrogenation of  $\text{CH}_4$  to  $\text{C}_2\text{H}_6$ . No enhancement was detected from either the partial oxidation or the oxidative dehydrogenation of methane using 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$  via UV-LED at a  $P(\text{O}_2)$  as high as 4.05 kPa, which indicated that the presence of large amounts of reactant oxygen may obliterate the effects of  $\text{O}_2^-$  due to the small amount of active oxygen.

Figure 2 shows the effect of UV-LED irradiation on the oxidative dehydrogenation of methane over  $\text{Sm}_2\text{O}_3$ ,  $\text{WO}_3$ , and 5 wt.%  $\text{WO}_3 + \text{Sm}_2\text{O}_3$  as a mixed-catalyst under the same reaction conditions as those used for obtaining the results shown in Figure 1. The specific surface areas of  $\text{WO}_3$  and 5 wt.%  $\text{WO}_3 + \text{Sm}_2\text{O}_3$  were 5 and 6  $\text{m}^2/\text{g}$ , respectively. As shown in Figure 2,  $\text{WO}_3$  produced CO alone via partial oxidation of methane regardless of the use of UV-LED irradiation while  $\text{O}_2$  conversion was increased from 6% to 13%. In the present case, the addition of 5 wt.%  $\text{WO}_3$  into  $\text{Sm}_2\text{O}_3$  did not completely mask the unique nature of  $\text{Sm}_2\text{O}_3$  in the oxidative coupling of methane. The effects of UV-LED irradiation on the catalytic activity of 5 wt.%  $\text{WO}_3 + \text{Sm}_2\text{O}_3$  were rather small. Slight decreases were detected for  $\text{CH}_4$  conversion,  $\text{C}_2$  yield,  $\text{C}_2\text{H}_6$  selectivity, CO selectivity, and  $\text{CO}_2$  selectivity together with slight increases in  $\text{O}_2$  conversion and  $\text{C}_2\text{H}_4$  selectivity that ranged from 12.2% to 12.9%. Therefore, the effect of  $\text{H}_2\text{O}_2$  generated by UV-LED irradiation on  $\text{WO}_3$  under a gaseous  $\text{O}_2$  atmosphere could have been negligible while those of  $\text{H}_2\text{O}_2$  seemed to slightly contribute to an acceleration of the oxidative dehydrogenation of  $\text{C}_2\text{H}_6$  to  $\text{C}_2\text{H}_4$ .



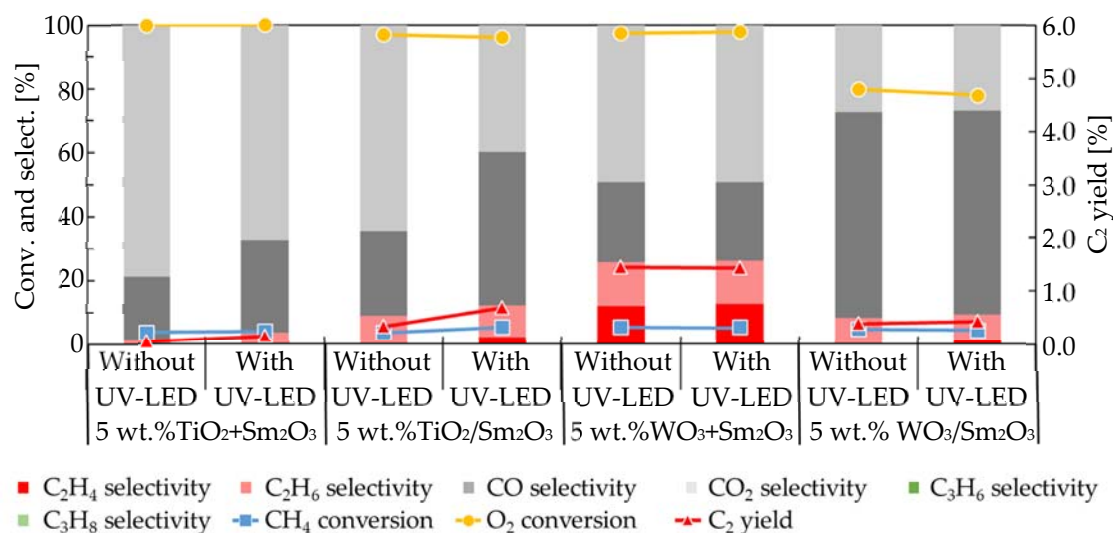
**Figure 1.** Effect of UV-LED irradiation on the oxidative dehydrogenation of methane when using  $\text{Sm}_2\text{O}_3$ ,  $\text{TiO}_2$ , and 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$ .



**Figure 2.** Effects of UV-LED irradiation on the oxidative dehydrogenation of methane when using  $\text{Sm}_2\text{O}_3$ ,  $\text{WO}_3$ , and 5 wt.%  $\text{WO}_3 + \text{Sm}_2\text{O}_3$ .

An effect from UV-LED irradiation was not evident when using mixed-catalysts. Therefore, supported-catalysts were used in the present study. In Figure 3, the use of UV-LED irradiation on the oxidative dehydrogenation of methane when using 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$  and 5 wt.%  $\text{WO}_3 + \text{Sm}_2\text{O}_3$  mixed-catalysts is compared with the results over 5 wt.%  $\text{TiO}_2/\text{Sm}_2\text{O}_3$  and 5 wt.%  $\text{WO}_3/\text{Sm}_2\text{O}_3$  supported-catalysts under the same reaction conditions as those used to obtain the results shown in Figures 1 and 2. The specific surface areas of supported-catalysts 5 wt.%  $\text{TiO}_2/\text{Sm}_2\text{O}_3$  and 5 wt.%  $\text{WO}_3/\text{Sm}_2\text{O}_3$  were 9 and 6  $\text{m}^2/\text{g}$ , respectively. Figure 3 compares the effect of UV-LED irradiation using 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$  with that using 5 wt.%  $\text{TiO}_2/\text{Sm}_2\text{O}_3$ , and the effect was more evident when using the supported catalyst. For example,  $\text{CH}_4$  conversion,  $\text{C}_2$  yield,  $\text{C}_2\text{H}_4$  selectivity,  $\text{C}_2\text{H}_6$  selectivity, and CO selectivity when using the supported catalyst all were enhanced by UV-LED irradiation from 3.6%, 0.3%, 0.0%, 9.0%, and 26.5% when using 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$  to 5.6%, 0.7%, 2.4%, 10.0%, and 47.7% when using 5 wt.%  $\text{TiO}_2/\text{Sm}_2\text{O}_3$ . By contrast, during deep oxidation,  $\text{CO}_2$  selectivity was suppressed by UV-LED irradiation from 64.4% to 39.8%. It is noteworthy that the catalytic activity on the 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$  catalyst (Figure 3) was higher than that of  $\text{TiO}_2$  itself, because activities such as the methane conversion and  $\text{C}_2$  selectivity on  $\text{Sm}_2\text{O}_3$  were higher than that on  $\text{TiO}_2$ , as shown in Figure 1. As shown in Figure 3, the conversions of both  $\text{CH}_4$  and  $\text{O}_2$  were insensitive to the irradiation

of UV-LED due to the oxygen-limiting conditions. It was evident that UV-LED irradiation enhanced the formation of C<sub>2</sub> compounds and CO and suppressed the deep oxidation to CO<sub>2</sub>. A comparison of the activity when using 5 wt.% WO<sub>3</sub> + Sm<sub>2</sub>O<sub>3</sub> with the use of 5 wt.% WO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub> revealed a negligible effect from UV-LED. Additionally, an increase in C<sub>2</sub>H<sub>4</sub> selectivity from 0.0% to 1.2% by UV-LED was detected when using 5 wt.% WO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub>, which was similar to the use of 5 wt.% WO<sub>3</sub> + Sm<sub>2</sub>O<sub>3</sub>, as shown in Figure 2.



**Figure 3.** Comparison of the effects of UV-LED irradiation of the oxidative dehydrogenation of methane when using 5 wt.% TiO<sub>2</sub> + Sm<sub>2</sub>O<sub>3</sub>, 5 wt.% TiO<sub>2</sub>/Sm<sub>2</sub>O<sub>3</sub>, 5 wt.% WO<sub>3</sub> + Sm<sub>2</sub>O<sub>3</sub>, and 5 wt.% WO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub>.

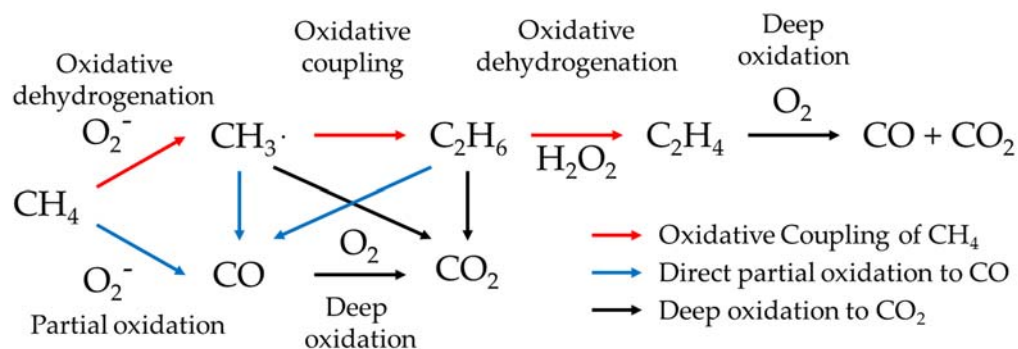
Based on Figure 3, the effect of UV-LED irradiation was more evident when using the supported-catalysts than when the mixed-catalysts were used. Table 1 summarizes the effect of UV-LED irradiation on the selectivities for CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> obtained from the oxidative dehydrogenation of methane over the mixed- and supported-catalysts using the data shown in Figure 3. The positive values in Table 1 indicate that the selectivity for each product was enhanced by UV-LED irradiation, while the negative values indicate that the selectivity was suppressed. Values less than 1.0 in Table 1 indicate that UV-LED irradiation had little effect on the corresponding selectivity.

**Table 1.** Effect of UV-LED irradiation on the selectivity for each of the products when using the binary catalysts in the present study.

Catalyst	$\Delta$ CO Selectivity [%]	$\Delta$ CO <sub>2</sub> Selectivity [%]	$\Delta$ C <sub>2</sub> H <sub>6</sub> Selectivity [%]	$\Delta$ C <sub>2</sub> H <sub>4</sub> Selectivity [%]
5 wt.% TiO <sub>2</sub> + Sm <sub>2</sub> O <sub>3</sub>	9.0	−11.4	2.4	Not detected
5 wt.% TiO <sub>2</sub> /Sm <sub>2</sub> O <sub>3</sub>	21.2	−24.6	1.0	2.4
5 wt.% WO <sub>3</sub> + Sm <sub>2</sub> O <sub>3</sub>	−0.3	−0.1	−0.2	0.7
5 wt.% WO <sub>3</sub> /Sm <sub>2</sub> O <sub>3</sub>	−0.7	−0.5	0.0	1.2

Although the effect of UV-LED irradiation was not evident for either 5 wt.% WO<sub>3</sub> + Sm<sub>2</sub>O<sub>3</sub> or 5 wt.% WO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub>, Table 1 is used here to discuss the effects of UV-LED irradiation. Active oxygen such as O<sub>2</sub><sup>−</sup> is generated when using both 5 wt.% TiO<sub>2</sub> + Sm<sub>2</sub>O<sub>3</sub> and 5 wt.% TiO<sub>2</sub>/Sm<sub>2</sub>O<sub>3</sub> due to the presence of TiO<sub>2</sub> in the binary catalysts [22]. When using these catalysts, the selectivities for CO, C<sub>2</sub>H<sub>6</sub>, and/or C<sub>2</sub>H<sub>4</sub> were improved by UV-LED irradiation, while the selectivity for CO<sub>2</sub> was suppressed. Therefore, the formation of O<sub>2</sub><sup>−</sup> by UV-LED when using the binary catalysts seems to have contributed to an enhancement of the formation of partial oxidation products, while the deep oxidation production of CO<sub>2</sub> was suppressed. When using 5 wt.% WO<sub>3</sub> + Sm<sub>2</sub>O<sub>3</sub> and 5 wt.% WO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub>, active oxygen such as H<sub>2</sub>O<sub>2</sub> is generated due to the presence of WO<sub>3</sub> in the binary catalysts [22]. Although the effect

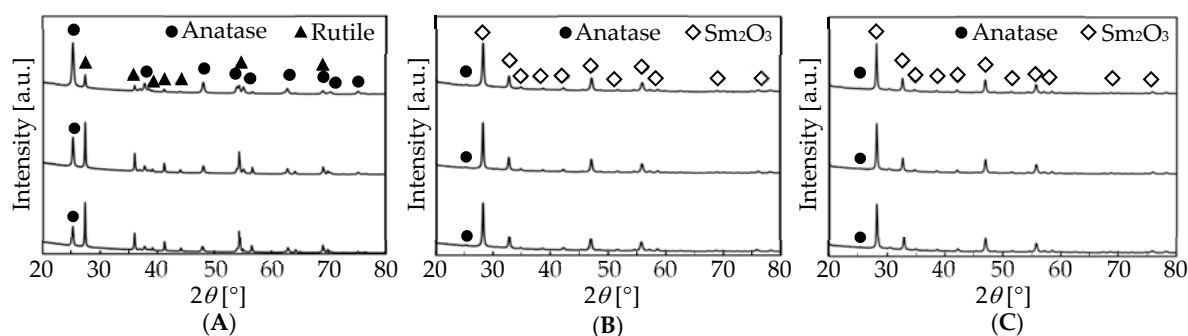
of UV-LED irradiation was rather small or negligible when using these catalysts compared with that when using TiO<sub>2</sub>-loading catalysts, a small but rather negligible enhancement of the selectivity to C<sub>2</sub>H<sub>4</sub> was detected with the use of 5 wt.% WO<sub>3</sub> + Sm<sub>2</sub>O<sub>3</sub> and 5 wt.% WO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub>. Therefore, the formation of H<sub>2</sub>O<sub>2</sub> from UV-LED when using these binary catalysts may slightly contribute to the oxidative dehydrogenation of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub>. Based on these results, it is possible to summarize the influence that active oxygen species exert on the present catalyst system, as shown in Scheme 3.



**Scheme 3.** Proposed contribution of active oxygen in the present binary catalysts.

The active oxygen of O<sub>2</sub><sup>-</sup> that formed when using TiO<sub>2</sub> + Sm<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>/Sm<sub>2</sub>O<sub>3</sub> contributed to the positive effect for the formations of CO, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub> together with a suppression of the deep oxidation of C<sub>2</sub>H<sub>4</sub> to CO and CO<sub>2</sub>. Furthermore, as shown in the results for TiO<sub>2</sub>, the O<sub>2</sub><sup>-</sup> formed on TiO<sub>2</sub> alone directly contributed to the partial oxidation of CH<sub>4</sub> to CO. The active oxygen of H<sub>2</sub>O<sub>2</sub> that formed when using both 5 wt.% WO<sub>3</sub> + Sm<sub>2</sub>O<sub>3</sub> and 5 wt.% WO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub> showed a negligible contribution to the conversion of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> via oxidative dehydrogenation. It should be noted that H<sub>2</sub>O<sub>2</sub> is an active species for other partial oxidations such as the epoxidation of alkenes. Therefore, the WO<sub>3</sub> system may be one of the most plausible candidates for the epoxidation of alkenes under UV-LED irradiation. Gaseous O<sub>2</sub> is the main contributor to the deep oxidation to CO<sub>2</sub>.

Finally, the catalysts used in the present study were analyzed using XRD. XRD patterns of the single oxides of Sm<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub> were matched to the reference patterns for the corresponding oxide (PDF 01-078-4055 and 01-083-0950, respectively; not shown). For 5 wt.% WO<sub>3</sub> + Sm<sub>2</sub>O<sub>3</sub> and 5 wt.% WO<sub>3</sub>/Sm<sub>2</sub>O<sub>3</sub>, the XRD peaks due to Sm<sub>2</sub>O<sub>3</sub> were detected alone (not shown). As shown in Figure 4A, before the reaction, TiO<sub>2</sub> was a mixture of anatase- and rutile-type TiO<sub>2</sub> (PDF 00-064-0863 and 01-086-0148, respectively). The anatase-type remained after the reaction, regardless of the UV-LED irradiation. Furthermore, Figure 4B,C shows that 5 wt.% TiO<sub>2</sub> + Sm<sub>2</sub>O<sub>3</sub> and 5 wt.% TiO<sub>2</sub>/Sm<sub>2</sub>O<sub>3</sub> contained a trace amount of anatase-type TiO<sub>2</sub> together with Sm<sub>2</sub>O<sub>3</sub> before the reaction. However, after the reaction with and without UV-LED irradiation, peaks due to Sm<sub>2</sub>O<sub>3</sub> were detected together with a trace amount of anatase-type TiO<sub>2</sub>. Based on these XRD results, we concluded that anatase-type TiO<sub>2</sub> remained during the reaction and the effect of UV-LED on the reaction came from the contribution of the anatase-type TiO<sub>2</sub> [25].



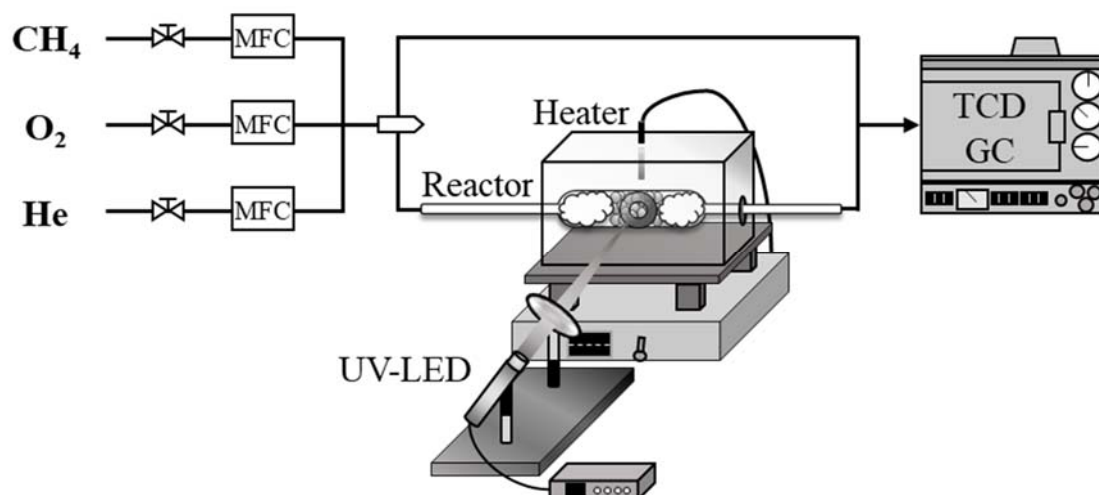
**Figure 4.** XRD of (A)  $\text{TiO}_2$ , (B) 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$ , and (C) 5 wt.%  $\text{WO}_3/\text{Sm}_2\text{O}_3$ . Upper—before the reaction. Middle and lower—after the reaction without and with UV-LED.

### 3. Materials and Methods

Mixed-catalysts ( $\text{TiO}_2 + \text{Sm}_2\text{O}_3$  and  $\text{WO}_3 + \text{Sm}_2\text{O}_3$ ) were prepared via the kneading of  $\text{Sm}_2\text{O}_3$  (Wako Pure Chemical Industries, Ltd., Osaka, Japan) with either  $\text{TiO}_2$  (JRC-TIO-15, a reference catalyst supplied from The Catalysis Society of Japan, Tokyo, Japan) or  $\text{WO}_3$  (Wako Pure Chemical Industries, Ltd.) for 30 min. For the preparation of 5 wt.%  $\text{TiO}_2 + \text{Sm}_2\text{O}_3$ , 0.018 g of  $\text{TiO}_2$  was kneaded with 0.350 g of  $\text{Sm}_2\text{O}_3$  for 30 min. Supported-catalysts ( $\text{TiO}_2/\text{Sm}_2\text{O}_3$  and  $\text{WO}_3/\text{Sm}_2\text{O}_3$ ) were prepared via impregnation. The preparation of 5 wt.%  $\text{TiO}_2/\text{Sm}_2\text{O}_3$  began with 20 mL of 2-propanol (Wako Pure Chemical Industries, Ltd.) into which we dissolved 0.592 g of titanium tetraisopropoxide (Wako Pure Chemical Industries, Ltd.) and 3.00 g of  $\text{Sm}_2\text{O}_3$ , followed by the further addition of 35 mL of distilled water. The resultant suspension was then evaporated and dried at 333 K for 24 h. Finally, the resultant solid was calcined at 973 K for 3 h. The preparation of 5 wt.%  $\text{WO}_3/\text{Sm}_2\text{O}_3$  began with 20 mL of aqueous solution into which we dissolved 0.174 g of ammonium (para)tungstate hydrate (Sigma-Aldrich Japan Co. LLC, Tokyo, Japan) and 3.00 g of  $\text{Sm}_2\text{O}_3$ . The resultant suspension was treated in a manner similar to the preparation of  $\text{TiO}_2/\text{Sm}_2\text{O}_3$ . In order to analyze those catalysts, X-ray diffraction (XRD) patterns were obtained using a SmartLab/R/INP/DX (Rigaku Co., Osaka Japan) with a  $\text{Cu K}\alpha$  radiation monochromator at 45 kV and 150 mA. In order to estimate the specific surface areas of those catalysts via BET, nitrogen adsorption isotherms of the catalysts pretreated at 473 K for 5 h were measured using a BELSORPmax12 (MicrotracBEL, Osaka, Japan) at 77 K.

The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor, which was placed in an electric furnace with an optical window, and operated at atmospheric pressure and 898 K (Scheme 4). As a light source for UV-LED irradiation, a Lightningcure LC-L1V3 (Hamamatsu Photonics K.K., Shizuoka, Japan) was used. This light source emits UV light at a wavelength of 365 nm for an average maximum irradiation intensity of 14,000  $\text{mW}/\text{cm}^2$  and a maximum output of 450 mW, which is sufficient for the activation of  $\text{O}_2$  when using  $\text{TiO}_2$  and  $\text{WO}_3$  under the present reaction conditions.

The temperature of the catalyst (0.350 g and 0.368 g for single and binary oxide catalysts, respectively) was increased to 898 K under a flow of He. After the reaction temperature was stabilized, the catalyst was treated with a flow of  $\text{O}_2$  (15 mL/min) for 1 h. Activity tests were then carried out under 15 mL/min of a reactant gas flow that consisted of  $\text{CH}_4$  and  $\text{O}_2$  diluted with He. In the present study, partial-pressure ratios of 7.1 and 14.2 were employed for  $\text{CH}_4/\text{O}_2$ , and the partial pressures were then adjusted to  $P(\text{CH}_4)/P(\text{O}_2) = 28.7 \text{ kPa}/4.05 \text{ kPa}$  and  $28.7 \text{ kPa}/2.03 \text{ kPa}$ . Under these conditions, homogeneous reactions were not detected. The reaction was monitored using an on-line gas chromatograph (GC-8APT, Shimadzu Corp., Kyoto, Japan) that involved the use of a thermal conductivity detector (TCD). The columns in the TCD-GC consisted of a Molecular Sieve 5A (0.3 m  $\times$   $\Phi$  3 mm) for the detection of  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  at 318 K and a Porapak Q (6 m  $\times$   $\Phi$  3 mm) for the detection of  $\text{CO}_2$ ,  $\text{C}_2$ , and  $\text{C}_3$  species at the column temperatures between 318 and 493 K with a heating rate of 10 K/min. The conversion and the selectivity were estimated on a carbon basis.



**Scheme 4.** Fixed-bed continuous-flow quartz reactor with UV-LED.

#### 4. Conclusions

In order to investigate the active oxygen effect that  $O_2^-$  and  $H_2O_2$  exert on the catalytic oxidative dehydrogenation of methane, binary oxide consisting of  $Sm_2O_3$ , which is an oxidative coupling catalyst for methane, and  $TiO_2$  or  $WO_3$ , which generate  $O_2^-$  or  $H_2O_2$ , respectively, when irradiated with UV-LED, were prepared using kneading and impregnation methods. Regardless of the preparation methods,  $O_2^-$  generated from  $TiO_2$  under UV-LED irradiation promoted the partial oxidation of methane to CO and oxidative conversion to  $C_2$  compounds, while it suppressed complete oxidation to  $CO_2$ . By contrast, regardless of the preparation methods,  $H_2O_2$  generated from  $WO_3$  under UV-LED irradiation had no evident effect on the oxidation of methane. It is noteworthy that the use of MgO instead of  $Sm_2O_3$  had no effect on the results of UV-LED irradiation. Therefore, it is suggested that the use of any oxide catalyst with great redox properties equal to those of  $Sm_2O_3$  would produce the above-mentioned advantageous effects via UV-LED irradiation.

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