Oxidative Dehydrogenation of Methane When Using TiO2- or WO3-Doped Sm2O3 in the Presence of Active Oxygen Excited with UV-LED

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Received: 14 April 2020; Accepted: 15 May 2020; Published: 18 May 2020

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 TiO2 or WO3, which generate active oxygen from UV-LED irradiation conditions under an oxygen flow. These photo-catalysts were studied in combination with Sm2O3, 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 TiO2 or WO3 were either supported on or kneaded with Sm2O3 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 Sm2O3 and TiO2 are used, while negligible UV-LED effects were detected when using Sm2O3 and WO3. These results indicate that with UV-LED irradiation the active oxygen of O2- from TiO2 certainly contributes to the activation of methane during the oxidative dehydrogenation of methane when using Sm2O3, while the active oxygen of H2O2 from WO3 under the same conditions afforded only negligible effects on the activation of methane.

Keywords: methane; oxidative dehydrogenation; active oxygen; UV-LED; TiO2; WO3; Sm2O3

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 C₂ 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 C₂ 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 C₂ hydrocarbons by a homogeneous gas-phase reaction (Scheme 1) [12–15]. Contributions have been proposed from active oxygen species such as O₂, OH, H₂O₂, or ¹O₂ (singlet oxygen) together with gas-phase oxygen (O₂) or catalytic lattice oxygen (O₂⁻), 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 (TiO₂) and tungsten oxide (WO₃) activate oxygen when electrons (e⁻) are excited by irradiation from an excitation light (UV-LED in the present study) and holes (h⁺) are sequentially generated, which results in the formation of active oxygen (Scheme 2).

Scheme 2. Production of active oxygen species via UV irradiation of TiO₂ and WO₃.
Based on Scheme 2, the oxidative dehydrogenation of methane was studied via contact with samarium oxide (Sm₂O₃; OCM-catalyst) and by examining the active oxygen species generated via irradiating UV-LED irradiation of either TiO₂ or WO₃ (photo-catalyst) under a gaseous O₂ atmosphere. It is generally accepted that O₂⁻ is generated from a one-electron reduction of TiO₂, and H₂O₂ is generated from a two-electron reduction of WO₃ [22]. When the active oxygen species derived from either TiO₂ or WO₃ contacted Sm₂O₃ 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 Sm₂O₃ together with TiO₂ or WO₃. Based on our preliminary experiments, the loading of photo-catalysts such as TiO₂ and WO₃ was fixed at 5 wt.%. First, the mixed-catalyst activity using 5 wt.% TiO₂ + Sm₂O₃ was tested together with that of either Sm₂O₃ or TiO₂. The specific surface areas of Sm₂O₃, TiO₂, and 5 wt.% TiO₂ + Sm₂O₃ were 7, 47, and 22 m²/g, respectively. Figure 1 shows the effect that UV-LED irradiation exerted on the oxidative dehydrogenation of methane at T = 898 K; P(CH₄) = 28.7 kPa; and P(O₂) = 2.03 kPa (P(CH₄)/P(O₂) = 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 Sm₂O₃ showed no advantageous effects on either C₂ yield or on the conversions of O₂ and CH₄, while CO selectivity was slightly changed from 9.4% to 10.5% by the irradiation. A similar effect of UV-LED on TiO₂ yielded CO selectivity of 83.8% to 85.2%. It should be noted that the conversions of CH₄ and O₂ were not influenced by the irradiation of UV-LED due to the oxygen-limiting conditions. When adding 5 wt.% TiO₂ into Sm₂O₃ (5 wt.% TiO₂ + Sm₂O₃), the unique nature of Sm₂O₃ that allows coupling with methane was mostly masked by the nature of TiO₂ that allows the partial oxidation of methane, and this resulted in a slight formation of C₂H₆ on 5 wt.% TiO₂ + Sm₂O₃. Furthermore, an evident improvement in CO selectivity of from 19.9% to 28.9% was detected followed by a suppression of CO₂ selectivity of from 78.6% to 67.2% after UV-LED irradiation of the mixed-catalyst. It should be noted that C₂H₆ selectivity was also slightly improved from 1.5% to 3.9% via UV-LED irradiation using 5 wt.% TiO₂ + Sm₂O₃. Therefore, O₂⁻ generated via the UV-LED irradiation of TiO₂ under a gaseous O₂ atmosphere seemed to contribute to the acceleration of the partial oxidation of CH₄ to CO together with the oxidative dehydrogenation of CH₄ to C₂H₆. No enhancement was detected from either the partial oxidation or the oxidative dehydrogenation of methane using 5 wt.% TiO₂ + Sm₂O₃ via UV-LED at a P(O₂) as high as 4.05 kPa, which indicated that the presence of large amounts of reactant oxygen may obliterate the effects of O₂⁻ due to the small amount of active oxygen.
Figure 1. Effect of UV-LED irradiation on the oxidative dehydrogenation of methane when using Sm$_2$O$_3$, TiO$_2$, and 5 wt.% TiO$_2$ + Sm$_2$O$_3$.

Figure 2 shows the effect of UV-LED irradiation on the oxidative dehydrogenation of methane over Sm$_2$O$_3$, WO$_3$, and 5 wt.% WO$_3$ + Sm$_2$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 WO$_3$ and 5 wt.% WO$_3$ + Sm$_2$O$_3$ were 5 and 6 m$^2$/g, respectively. As shown in Figure 2, WO$_3$ produced CO alone via partial oxidation of methane regardless of the use of UV-LED irradiation while O$_2$ conversion was increased from 6% to 13%. In the present case, the addition of 5 wt.% WO$_3$ into Sm$_2$O$_3$ did not completely mask the unique nature of Sm$_2$O$_3$ in the oxidative coupling of methane. The effects of UV-LED irradiation on the catalytic activity of 5 wt.% WO$_3$ + Sm$_2$O$_3$ were rather small. Slight decreases were detected for CH$_4$ conversion, C$_2$ yield, C$_3$H$_6$ selectivity, CO selectivity, and CO$_2$ selectivity together with slight increases in O$_2$ conversion and C$_2$H$_4$ selectivity that ranged from 12.2% to 12.9%. Therefore, the effect of H$_2$O$_2$ generated by UV-LED irradiation on WO$_3$ under a gaseous O$_2$ atmosphere could have been negligible while those of H$_2$O$_2$ seemed to slightly contribute to an acceleration of the oxidative dehydrogenation of C$_3$H$_6$ to C$_2$H$_4$. 
Figure 2. Effects of UV-LED irradiation on the oxidative dehydrogenation of methane when using Sm$_2$O$_3$, WO$_3$, and 5 wt.% WO$_3$+Sm$_2$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.% TiO$_2$+Sm$_2$O$_3$ and 5 wt.% WO$_3$+Sm$_2$O$_3$ mixed-catalysts is compared with the results over 5 wt.% TiO$_2$/Sm$_2$O$_3$ and 5 wt.% WO$_3$/Sm$_2$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.% TiO$_2$/Sm$_2$O$_3$ and 5 wt.% WO$_3$/Sm$_2$O$_3$ were 9 and 6 m$^2$/g, respectively. Figure 3 compares the effect of UV-LED irradiation using 5 wt.% TiO$_2$+Sm$_2$O$_3$ with that using 5 wt.% TiO$_2$/Sm$_2$O$_3$, and the effect was more evident when using the supported catalyst. For example, CH$_4$ conversion, C$_2$ yield, C$_2$H$_4$ selectivity, C$_2$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.% TiO$_2$+Sm$_2$O$_3$ to 5.6%, 0.7%, 2.4%, 10.0%, and 47.7% when using 5 wt.% TiO$_2$/Sm$_2$O$_3$. By contrast, during deep oxidation, 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.% TiO$_2$ + Sm$_2$O$_3$ catalyst (Figure 3) was higher than that of TiO$_2$ itself, because activities such as the methane conversion and C$_2$ selectivity on Sm$_2$O$_3$ were higher than that on TiO$_2$, as shown in Figure 1. As shown in Figure 3, the conversions of both CH$_4$ and 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$_2$ compounds and CO and suppressed the deep oxidation to CO$_2$. A comparison of the activity when using 5 wt.% WO$_3$+Sm$_2$O$_3$ with the use of 5 wt.% WO$_3$/Sm$_2$O$_3$ revealed a negligible effect from UV-LED. Additionally, an increase in C$_2$H$_4$ selectivity from 0.0% to 1.2% by UV-LED was detected when using 5 wt.% WO$_3$/Sm$_2$O$_3$, which was similar to the use of 5 wt.% WO$_3$+Sm$_2$O$_3$, 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$_2$+Sm$_2$O$_3$, 5 wt.% TiO$_2$/Sm$_2$O$_3$, 5 wt.% WO$_3$+Sm$_2$O$_3$, and 5 wt.% WO$_3$/Sm$_2$O$_3$.

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$_2$, C$_2$H$_4$, and C$_2$H$_6$ 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.

| Catalyst                          | ∆CO Selectivity [%] | ∆CO₂ Selectivity [%] | ∆C₂H₆ Selectivity [%] | ∆C₂H₄ Selectivity [%] |
|-----------------------------------|---------------------|----------------------|-----------------------|-----------------------|
| 5 wt.% TiO₂ + Sm₂O₃              | 9.0                 | -11.4                | 2.4                   | Not detected          |
| 5 wt.% TiO₂/Sm₂O₃                | 21.2                | -24.6                | 1.0                   | 2.4                   |
| 5 wt.% WO₃ + Sm₂O₃               | -0.3                | -0.1                 | -0.2                  | 0.7                   |
| 5 wt.% WO₃/Sm₂O₃                 | -0.7                | -0.5                 | 0.0                   | 1.2                   |

Although the effect of UV-LED irradiation was not evident for either 5 wt.% WO₃ + Sm₂O₃ or 5 wt.% WO₃/Sm₂O₃, Table 1 is used here to discuss the effects of UV-LED irradiation. Active oxygen such as O₂⁻ is generated when using both 5 wt.% TiO₂ + Sm₂O₃ and 5 wt.% TiO₂/Sm₂O₃ due to the presence of TiO₂ in the binary catalysts [22]. When using these catalysts, the selectivities for CO, C₂H₆, and/or C₂H₄ were improved by UV-LED irradiation, while the selectivity for CO₂ was suppressed. Therefore, the formation of O₂⁻ 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 CO₂ was suppressed. When using 5 wt.% WO₃ + Sm₂O₃ and 5 wt.% WO₃/Sm₂O₃, active oxygen such as H₂O₂ is generated due to the presence of WO₃ 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 TiO₂-loading catalysts, a small but rather negligible enhancement of the selectivity to C₂H₄ was detected with the use of 5 wt.% WO₃ + Sm₂O₃ and 5 wt.% WO₃/Sm₂O₃. Therefore, the formation of H₂O₂ from UV-LED when using these binary catalysts may slightly contribute to the oxidative dehydrogenation of C₂H₆ to C₂H₄. 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 O₂⁻ that formed when using TiO₂ + Sm₂O₃ and TiO₂/Sm₂O₃ contributed to the positive effect for the formations of CO, C₂H₆, and C₂H₄ together with a suppression of the deep oxidation of C₂H₄ to CO and CO₂. Furthermore, as shown in the results for TiO₂, the O₂⁻ formed on TiO₂ alone directly contributed to the partial oxidation of CH₄ to CO. The active oxygen of H₂O₂ that formed when using both 5 wt.% WO₃ + Sm₂O₃ and 5 wt.% WO₃/Sm₂O₃ showed a negligible contribution to the conversion of C₂H₆ to C₂H₄ via oxidative dehydrogenation. It should be noted that H₂O₂ is an active species for other partial oxidations such as the epoxidation of alkenes. Therefore, the WO₃ system may be one of the most plausible candidates for the epoxidation of alkenes under UV-LED irradiation. Gaseous O₂ is the main contributor to the deep oxidation to CO₂.
Finally, the catalysts used in the present study were analyzed using XRD. XRD patterns of the single oxides of Sm$_2$O$_3$ and WO$_3$ 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$_3$ + Sm$_2$O$_3$ and 5 wt.% WO$_3$/Sm$_2$O$_3$, the XRD peaks due to Sm$_2$O$_3$ were detected alone (not shown). As shown in Figure 4 (A), before the reaction, TiO$_2$ was a mixture of anatase- and rutile-type TiO$_2$ (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$_2$ + Sm$_2$O$_3$ and 5 wt.% TiO$_2$/Sm$_2$O$_3$ contained a trace amount of anatase-type TiO$_2$ together with Sm$_2$O$_3$ before the reaction. However, after the reaction with and without UV-LED irradiation, peaks due to Sm$_2$O$_3$ were detected together with a trace amount of anatase-type TiO$_2$. Based on these XRD results, we concluded that anatase-type TiO$_2$ remained during the reaction and the effect of UV-LED on the reaction came from the contribution of the anatase-type TiO$_2$ [25].

![Figure 4. XRD of (A) TiO$_2$, (B) 5 wt.% TiO$_2$ + Sm$_2$O$_3$, and (C) 5 wt.% WO$_3$/Sm$_2$O$_3$. Upper—before the reaction. Middle and lower—after the reaction without and with UV-LED.](image-url)

3. Materials and Methods

Mixed-catalysts (TiO$_2$ + Sm$_2$O$_3$ and WO$_3$ + Sm$_2$O$_3$) were prepared via the kneading of Sm$_2$O$_3$ (Wako Pure Chemical Industries, Ltd., Osaka, Japan) with either TiO$_2$ (JRC-TIO-15, a reference catalyst supplied from The Catalysis Society of Japan, Tokyo, Japan) or WO$_3$ (Wako Pure Chemical Industries, Ltd.) for 30 min. For the preparation of 5 wt.% TiO$_2$ + Sm$_2$O$_3$, 0.018 g of TiO$_2$ was kneaded with 0.350 g of Sm$_2$O$_3$ for 30 min. Supported-catalysts (TiO$_2$/Sm$_2$O$_3$ and WO$_3$/Sm$_2$O$_3$) were prepared via impregnation. The preparation of 5 wt.% TiO$_2$/Sm$_2$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 Sm$_2$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.% WO$_3$/Sm$_2$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 Sm$_2$O$_3$. The resultant suspension was treated in a manner similar to the preparation of TiO$_2$/Sm$_2$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 Cu Kα 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 mW/cm$^2$ and a maximum output of 450 mW, which is sufficient for the activation of O$_2$ when using TiO$_2$ and 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 O₂ (15 mL/min) for 1 h. Activity tests were then carried out under 15 mL/min of a reactant gas flow that consisted of CH₄ and O₂ diluted with He. In the present study, partial-pressure ratios of 7.1 and 14.2 were employed for CH₄/O₂, and the partial pressures were then adjusted to P(CH₄)/P(O₂) = 28.7 kPa/4.05 kPa and 28.7 kPa/2.03 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 × Φ 3 mm) for the detection of O₂, CO, and CH₄ at 318 K and a Porapak Q (6 m × Φ 3 mm) for the detection of CO₂, C₂, and C₃ 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.

4. Conclusions

In order to investigate the active oxygen effect that O₂⁻ and H₂O₂ exert on the catalytic oxidative dehydrogenation of methane, binary oxide consisting of Sm₂O₃, which is an oxidative coupling catalyst for methane, and TiO₂ orWO₃, which generate O₂⁻ or H₂O₂, respectively, when irradiated with UV-LED, were prepared using kneading and impregnation methods. Regardless of the preparation methods, O₂⁻ generated from TiO₂ under UV-LED irradiation promoted the partial oxidation of methane to CO and oxidative conversion to C₂ compounds, while it suppressed complete oxidation to CO₂. By contrast, regardless of the preparation methods, H₂O₂ generated from WO₃ under UV-LED irradiation had no evident effect on the oxidation of methane. It is noteworthy that the use of MgO instead of Sm₂O₃ 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 Sm₂O₃ would produce the above-mentioned advantageous effects via UV-LED irradiation.

Author Contributions: Conceptualization and methodology, S.S., A.F., Y.K., and W.N.; validation, Y.H., I.O., N.S., and M.K.; formal analysis and investigation, S.S., Y.Y., and I.O.; writing—original draft preparation, S.S.; writing—review and editing, S.S., N.S., M.K., A.F., Y.K., and W.N.; and, supervision, S.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by JSPS KAKENHI Grant Number JP17K19014 and by the Research Clusters Program of Tokushima University (1702001).

Acknowledgments: The authors gratefully acknowledge Toshihiro Okamoto of the Institute of Post-LED Photonics, Tokushima University for his valuable suggestions concerning photo-catalysts.

Conflicts of Interest: The authors declare no conflicts of interest.
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