Dry reforming of methane, shown in (1), is an endothermic reaction that usually requires high temperature to proceed. Since the use of photoenergy can lower the reaction temperature in many cases, in the present study we investigated the photocatalytic conversion of CH\(_4\) in the presence of CO\(_2\) at various reaction temperatures.

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 & \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta G_{298 \text{ K}} = 170 \text{ kJ mol}^{-1} \quad (1) \\
2\text{CH}_4 & \rightarrow \text{C}_2\text{H}_6 + \text{H}_2 \quad \Delta G_{298 \text{ K}} = 68.8 \text{ kJ mol}^{-1} \quad (2).
\end{align*}
\]

\(\beta\)-Ga\(_2\)O\(_3\), which was active for photocatalytic non-oxidative of methane coupling,\(^1\) shown in (2), was used as the photocatalyst. A mixture of CH\(_4\) and CO\(_2\) was introduced at various temperatures and the Ga\(_2\)O\(_3\) was irradiated by a Xe lamp for 3 h.

Without CO\(_2\), only reaction (2) proceeded around room temperature producing mainly C\(_2\)H\(_6\) and H\(_2\). In the presence of CO\(_2\), besides coupling products, a trace amount of CO was also detected. The amounts of H\(_2\), coupling products, and CO increased at higher reaction temperature (473 K). From the stoichiometry of the products and since the products could not be obtained in the dark and/or without photocatalyst, it was suggested that the reactions (1) and (2) mainly proceeded photocatalytically over Ga\(_2\)O\(_3\). Since CO product increased while hydrocarbons products (C\(_\geq2\)) decreased as the reaction temperature increased, selectivity to CO product was higher at the higher reaction temperature, such as 94% at 773 K.

Without UV irradiation, reactions (1) and (2) did not occur below 773 K. While only a very trace amount of coupling products was obtained, CO could be detected at 773 K or higher in the dark, as shown in Fig.1. At the same temperatures, the amount of CO produced under UV irradiation was much higher than that produced in the dark, suggesting that a kind of synergic effect between photoenergy and thermal energy would contribute to the activity of Ga\(_2\)O\(_3\) for the CO formation.

![Fig. 1](attachment:image.png)

**Fig. 1** Effect of reaction temperature on (a) hydrocarbons products under UV irradiation, (b) CO product under UV irradiation, and (c) CO product in the dark.

(1) L. Yuliati et al., 98 回触媒討論会(A), 3K14.