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Kyoto University
Photocatalytic Reduction of CO$_2$ using H$_2$ as Reductant over ATaO$_3$ photocatalysts (A = Li, Na, K)

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ATaO$_3$ (A = Li, Na, K) compound oxides exhibit photocatalytic activity for the reduction of CO$_2$ in the presence of H$_2$. Only CO gas was generated over all samples under photoirradiation. The photocatalytic activity was higher in the order corresponding to KTaO$_3$, NaTaO$_3$ and LiTaO$_3$ (LiTaO$_3$ > NaTaO$_3$ > KTaO$_3$). The order of the photocatalytic activities was consistent with that of the $E_g$ (optical gap) values. After 24 h of photoirradiation, the amount of evolved CO reached 0.42 µmol·g$^{-1}$ over LiTaO$_3$. TPD experiments indicated that the broad peak which is assigned to chemisorbed CO$_2$ gas was observed at 573 K in the case of LiTaO$_3$. On the contrary, there was no peak in the spectra of NaTaO$_3$ and KTaO$_3$. The amount of evolved CO gas almost strongly depends on amount of chemisorbed CO$_2$ in the case of ATaO$_3$ (A = Li, Na, K). In addition, the photocatalytic activity increased with increasing the calcination temperature of LiTaO$_3$. This means that a smooth charge separation in a LiTaO$_3$ photocatalyst and chemisorption of CO$_2$ on the surface contribute to effective reduction of CO$_2$ in the presence of H$_2$. 
Introduction

Recently, many countries that have approved the ratification of the Kyoto Protocol are enforcing strict regulations on carbon dioxide (CO$_2$) emission to meet international environmental standards. These countries are reducing CO$_2$ emission in many different ways, for example, by storage in the ground and sea, absorption into various functionalized materials, and large-scale forestation. However, it is important to develop the technique to chemically convert CO$_2$ into harmless compounds or other chemical products in the future. Chemical fixation of CO$_2$ in the presence of a heterogeneous photocatalyst is a promising method for converting it into other carbon sources such as carbon monoxide (CO), formaldehyde (HCHO), formic acid (HCOOH), methanol (CH$_3$OH), and methane (CH$_4$)[1]. In the 1980s, the effect of H$_2$O as a reductant on heterogeneous photocatalysts used for the photocatalytic reduction of CO$_2$ attracted considerable interest[2, 3].

We have found that CO is generated as a result of the photocatalytic reduction of CO$_2$ in the presence of H$_2$ or CH$_4$ as a reductant over ZrO$_2$[4-9], Rh/TiO$_2$[10, 11], MgO[12, 13], and Ga$_2$O$_3$[14]. With the exception of Rh/TiO$_2$, these solid materials exhibit the properties of solid base catalysts; therefore, CO$_2$ can be adsorbed on the surface of these materials. We have insisted on the importance of CO$_2$ adsorption on the surface because this makes CO$_2$, which is a stable and linear molecular, into an active species which provides abundant reactivity for the photocatalytic reduction of CO$_2$. As mentioned above, it was reported that the photocatalytic reduction CO$_2$ in the presence of H$_2$ proceeds over many simple oxides such as ZrO$_2$, MgO, and Ga$_2$O$_3$. However, there is no report that a compound oxide exhibits photocatalytic activity for the
reduction of CO₂. In the field of water splitting, many compound oxides are known to function as an effective photocatalyst. Among them, Kudo et al.[15, 16] reported that La doped NaTaO₃ shows incredible photocatalytic activity for overall water splitting. In this study, we first found that ATaO₃ (A = Li, Na, K) as a compound oxide is a candidate of photocatalyst for the reduction of CO₂.

**Experimental section**

ATaO₃ (A = Li, Na, K) samples used in this study were synthesized by a conventional solid state reaction (SSR) method. A stoichiometric mixture of Ta₂O₅ and A₂CO₃ (A = Li, Na, K) was calcinated at 1373 K for 20 h in the atmosphere in a programmable box furnace. A 5mol% excess of A₂CO₃ (A = Li, Na, K) was used to counteract loss of alkali as an oxide vapor during the heating circle. X-ray diffraction pattern (XRD) of an ATaO₃ (A = Li, Na, K) photocatalyst was measured by a Rigaku Multi Flex powder X-ray diffractometer. Kr adsorption isotherm was obtained using a BELSORP 28SA-SP system supplied by the BEL Japan Inc. The specific surface area was calculated from Kr adsorption isotherm of ATaO₃ (A = Li, Na, K) using the Brunauer-Emment-Teller (BET) method because the specific surface area is too small to be estimated by N₂ adsorption isotherm. Scanning electron microscope (SEM) images were obtained on a Hitachi S-4700 scanning electron microscope. UV-Vis diffuse reflectance (UV-Vis. DR) spectra were obtained using a JASCO Corporation V-670 diffused reflectance spectrometer with an integrating sphere at room temperature. BaSO₄ was used as a standard reflection sample. Temperature programmed desorption (TPD) profile was recorded by a TPD-1-AT instrument supplied by the BEL Japan Inc.
The photocatalytic reduction was carried out in a closed circulating system connected to a vacuum line. 2.0 g of ATaO₃ (A = Li, Na, K) was spread on the flat bottom (50 φ) of a quartz reactor (dead space: 150 mL). The catalyst sample was heated and evacuated at 673 K and then treated with O₂ (80 kPa) for 60 min, followed by evacuation for 2 h at the same temperature. The purified CO₂ (150 µmol) as a substrate and H₂ (50 µmol) as a reductant were admitted to the reactor after the pretreatment. The ATaO₃ (A = Li, Na, K) sample was illuminated throughout a range of wavelength from the bottom of the reactor with a 200 W Hg-Xe lamp (SAN-EI ELECTRIC CO., LTD, UVF-204S Type C). The reaction temperature increased to 303 K after photoirradiation because of heat of the light source. The analysis of products was performed with TCD gas chromatograph (Shimadzu GC-8A) equipped with a column packed with active carbon and with helium (He) as a carrier gas.

Results and Discussion

The prepared ATaO₃ (A = Li, Na, K) powders were qualitatively analyzed by some conventional method of analysis for a photocatalyst (XRD, SEM, and UV-Vis. spectroscopy). Figure 1 shows the XRD patterns of ATaO₃ (A = Li, Na, K). The peak assigned to impurities did not appear in all XRD patterns. All of ATaO₃ consist of corner-sharing TaO₆ octahedra with ilmenite (LiTaO₃) and perovskite (NaTaO₃ and KTaO₃) like structures. The morphology of synthesized ATaO₃ (A = Li, Na, K) was observed by SEM as shown in Figure 2. All prepared samples had fine primary particles with an average diameter of 1–3 µm. The BET specific surface area of ATaO₃ (A = Li, Na, K) estimated by the Kr adsorption isotherm are 0.28, 0.10, and 0.10 m²·g⁻¹,
respectively. The UV-Vis. DR spectra of ATaO₃ (A = Li, Na, K) were obtained after converting reflection coefficient, \( R \) to \( F(R_\infty) \) by Kubelka-Munk function, \( F(R_\infty) = (1-R^2)/2R \) as shown in Figure 3. Generally, \( E_g \) (optical gap) values are derived from optical absorption spectra and diffuse reflectance spectra. In the case of Devis-Mott’s method, the \( E_g \) values are derived from the equation following 

\[
F(R_\infty) \cdot h \nu \propto (h \nu - E_g)^n,
\]

where \( n = 2, 3, 1/2 \) and \( 3/2 \) for indirect allowed, indirect forbidden, direct allowed, and direct forbidden transitions, respectively. The \( E_g \) values of ATaO₃ (A = Li, Na, K) are estimated to 4.9, 4.1 and 3.7 eV by Davis-Mott’s method with \( n = 1/2 \) (direct allowed)[17, 18].

Figure 4 shows the amount of evolved CO gas for the photocatalytic reduction of CO₂ in the presence of H₂ as a reductant over ATaO₃ (A = Li, Na, K) after 24 h of photoirradiation. We obviously confirmed that the reaction does not proceed in the absence of ATaO₃ or in the dark. The photocatalytic reduction of CO₂ proceeded over all ATaO₃ (A = Li, Na, K) samples. CO gas was evolved over all ATaO₃ (A = Li, Na, K) samples under photoirradiation and the other compounds (for example, HCOOH, HCHO, CH₃OH, and CH₄) were not produced in the gas phase. LiTaO₃ exhibits the highest activity in the ATaO₃ (A = Li, Na, K) samples. The photocatalytic activity was higher in the order corresponding to KTaO₃, NaTaO₃ and LiTaO₃ (LiTaO₃ > NaTaO₃ > KTaO₃). Amount of evolved CO gas over LiTaO₃ was eight times higher than that over KTaO₃. No product was observed over LiTaO₃ under photoirradiation \( \lambda > 310 \) nm using a UV-29 cut-off filter. Therefore, the electron transition between band gap energy is concerned in the photocatalytic reduction of CO₂ over LiTaO₃. The order of the photocatalytic activities was consistent with that of the \( E_g \) (optical gap) values as
described above. Kato and Kudo[15] concluded that the conduction band levels and the transferring excited energy contribute to photocatalytic activities of naked alkali tantalate photocatalysts and a surface area is not an important factor for overall water splitting because a LiTaO₃ photocatalyst showed the highest activity for overall water splitting among the naked alkali tantalate photocatalysts prepared in the presence of excess alkali and the order of the activities was LiTaO₃ > NaTaO₃ > KTaO₃. In our case, it is expected that the conduction band levels and the transferring excited energy influence the photocatalytic activity for the photocatalytic reduction of CO₂.

It was reported that solid base materials such as ZrO₂, MgO, CaO, Al₂O₃ and Ga₂O₃ which possess base sites on the surface exhibit photocatalytic activity for the photocatalytic reduction of CO₂ in the presence of H₂. CO₂ is able to be adsorbed on the base site easily, and then the conformation of a linear CO₂ molecule undergoes a great change. The adsorption of CO₂ contributes to the photocatalytic reduction of CO₂. Figure 5 shows the CO₂-TPD spectra (m/z = 44) of A TaO₃ (A = Li, Na, K) after pretreatment at 673 K and CO₂ adsorption at room temperature. A broad peak was observed at 573 K in the case of LiTaO₃, although there was no peak in the spectra of NaTaO₃ and KTaO₃. It is known that Li₂CO₃ is decomposed at 900 K (heat decomposition). In fact, we obtained the same result as the reference. Accordingly, the peak at 573 K is assigned to not decomposition of Li₂CO₃ but desorption of a CO₂ molecule adsorbed on LiTaO₃. The adsorption isotherm of CO₂ was observed after pretreatment at 673 K as shown in Figure 6a. After that, CO₂ was adsorbed on LiTaO₃ after evacuation at room temperature again as shown in Figure 6b. These adsorption isotherms are expressed as a function of the Langmuir adsorption isotherm. Amount of
adsorbed CO\textsubscript{2} was saturated when equilibrium pressure is more than 0.96 kPa. The subtraction between panels a and b was 0.75 \( \mu \text{mol} \cdot \text{g}^{-1} \). The equilibrium pressure was about 2.7 kPa when 150 \( \mu \text{mol} \) of CO\textsubscript{2} was admitted to the reactor with 2.0 g of LiTaO\textsubscript{3} after the pretreatment. Thus, the amount of CO\textsubscript{2} physisorbed and chemisorbed on LiTaO\textsubscript{3} corresponds to 2.76 and 1.50 \( \mu \text{mol} \) under the reaction condition, respectively. Figure 7 demonstrates the amount of chemisorbed CO\textsubscript{2} on ATaO\textsubscript{3} (A = Li, Na, K). Amount of evolved CO gas almost depends on amount of chemisorbed CO\textsubscript{2} in the case of ATaO\textsubscript{3} (A = Li, Na, K) as well as the other reported materials such as ZrO\textsubscript{2}, MgO, and Ga\textsubscript{2}O\textsubscript{3}.

We have reported that MgO exhibits the best photocatalytic activity for the reduction of CO\textsubscript{2} in the presence of H\textsubscript{2} as a reductant under UV light irradiation. It is clarified that the photoactive site of MgO is compatible with the CO\textsubscript{2} adsorption site. The amount of evolved CO gas over MgO (12.9 \( \mu \text{mol} \cdot \text{g}^{-1} \)) is thirty-first higher than that over LiTaO\textsubscript{3} (0.42 \( \mu \text{mol} \cdot \text{g}^{-1} \)) under 24 h of photoirradiation using the same light source. On the other hand, amount of chemisorbed CO\textsubscript{2} gas over MgO (130 \( \mu \text{mol} \cdot \text{g}^{-1} \)) is enormous as compared to that on LiTaO\textsubscript{3} (0.75 \( \mu \text{mol} \cdot \text{g}^{-1} \))[12, 13]. Accordingly, the photoactive site of LiTaO\textsubscript{3} would be able to reduce adsorbed CO\textsubscript{2} to CO under photoirradiation effectively. We speculate that a smooth charge separation in LiTaO\textsubscript{3} contributes to the effective photocatalytic reduction of CO\textsubscript{2} in the presence of H\textsubscript{2}. Generally, the high crystallinity of photocatalyst is known to provide the smooth charge separation. In our case, the photocatalytic activity increased with increasing the calcination temperature of LiTaO\textsubscript{3} despite decreasing the specific surface area as shown in Figure 8. The BET specific surface area of LiTaO\textsubscript{3} calcined at 973, 1173, and 1373 K
are 1.1, 0.77, and 0.28 m²·g⁻¹, respectively. On the other hand, all peaks in the XRD pattern of LiTaO₃ became sharper and higher with increasing the calcination temperature. In this study, we found that some compound oxides such as ATaO₃ (A = Li, Na, K) exhibit the photocatalytic activity for the photocatalytic reduction of CO₂ in the presence of H₂ and expanded the capability of the effective CO₂ photocatalytic reduction system using high crystallinity of LiTaO₃; however the observed activity is very low. High specific surface area of LiTaO₃ is now under investigation and preparation.

**Conclusion**

It is found that photocatalytic reduction of CO₂ using H₂ as a reductant proceeds over ATaO₃ (A = Li, Na, K). CO gas was evolved over all ATaO₃ (A = Li, Na, K) samples under photoirradiation and the other compounds were not produced in the gas phase. LiTaO₃ exhibits the highest activity in the ATaO₃ (A = Li, Na, K) samples. The photocatalytic activity was higher in the order corresponding to KTaO₃, NaTaO₃ and LiTaO₃ (LiTaO₃ > NaTaO₃ > KTaO₃). The order of the photocatalytic activities was consistent with that of the $E_g$ (optical gap) values. Amount of evolved CO gas almost depends on amount of chemisorbed CO₂ in the case of ATaO₃. The photoactive site of LiTaO₃ would be able to capture CO₂ in the gas phase and reduce the adsorbed CO₂ to CO under photoirradiation effectively as compared to that of NaTaO₃ and KTaO₃.

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References and Notes


Figure captions

Figure 1  XRD patterns of ATaO₃ (A = Li, Na, K): (a) LiTaO₃, (b) NaTaO₃ and (c) KTaO₃

Figure 2  SEM images of ATaO₃ (A = Li, Na, K) : (a) LiTaO₃, (b) NaTaO₃ and (c) KTaO₃

Figure 3  UV-Vis. DR spectra of ATaO₃ (A = Li, Na, K) : (a) LiTaO₃, (b) NaTaO₃ and (c) KTaO₃

Figure 4  Amount of evolved CO gas for the photocatalytic reduction of CO₂ in the presence of H₂ as a reductant over ATaO₃ (A = Li, Na, K) after 24 h of photoirradiation

Figure 5  CO₂-TPD spectra (m/z = 44) of ATaO₃ (A = Li, Na, K) after pretreatment at 673 K and CO₂ adsorption at room temperature

Figure 6  The adsorption isotherms of CO₂ on LiTaO₃ (a) after pretreatment at 673 K, and then (b) after adsorption of CO₂ and evacuation at room temperature.

Figure 7  Amount of chemisorbed CO₂ on ATaO₃ (A = Li, Na, K).

Figure 8  Amount of evolved CO gas for the photocatalytic reduction of CO₂ in the presence of H₂ as a reductant over LiTaO₃ calcined at (a) 1373, (b) 973, and (c) 773 K after 24 h of photoirradiation.
Figure 1
Figure 2
Figure 3
Figure 4

Amount of evolved CO$_2$ gas/μmol g$^{-1}$

LiTaO$_3$, NaTaO$_3$, KTaO$_3$
Figure 5
Figure 6

(a)

(b)

Equilibrium pressure / kPa

Amount of adsorbed CO₂ / μmol g⁻¹
Figure 7

The diagram shows the amount of chemisorbed CO$_2$ in $\mu$mol g$^{-1}$ for different compounds: LiTaO$_3$, NaTaO$_3$, and KTaO$_3$. The amount of chemisorbed CO$_2$ is highest for LiTaO$_3$, followed by KTaO$_3$ and then NaTaO$_3$. The y-axis represents the amount of chemisorbed CO$_2$ in $\mu$mol g$^{-1}$, ranging from 0.0 to 1.0.
Figure 8