

Photocatalytic Reduction of CO₂ using H₂ as Reductant over ATaO₃ photocatalysts (A = Li, Na, K)

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Abstract

ATaO₃ (A = Li, Na, K) compound oxides exhibit photocatalytic activity for the reduction of CO₂ in the presence of H₂. Only CO gas was generated over all samples under photoirradiation. 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. After 24 h of photoirradiation, the amount of evolved CO reached 0.42 μmol·g⁻¹ over LiTaO₃. TPD experiments indicated that the broad peak which is assigned to chemisorbed CO₂ gas was observed at 573 K in the case of LiTaO₃. On the contrary, there was no peak in the spectra of NaTaO₃ and KTaO₃. The amount of evolved CO gas almost strongly depends on amount of chemisorbed CO₂ in the case of ATaO₃ (A = Li, Na, K). In addition, the photocatalytic activity increased with increasing the calcination temperature of LiTaO₃. This means that a smooth charge separation in a LiTaO₃ photocatalyst and chemisorption of CO₂ on the surface contribute to effective reduction of CO₂ in the presence of H₂.

Introduction

Recently, many countries that have approved the ratification of the Kyoto Protocol are enforcing strict regulations on carbon dioxide (CO₂) emission to meet international environmental standards. These countries are reducing CO₂ 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 CO₂ into harmless compounds or other chemical products in the future. Chemical fixation of CO₂ 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 (CH₃OH), and methane (CH₄)[1]. In the 1980s, the effect of H₂O as a reductant on heterogeneous photocatalysts used for the photocatalytic reduction of CO₂ attracted considerable interest[2, 3].

We have found that CO is generated as a result of the photocatalytic reduction of CO₂ in the presence of H₂ or CH₄ as a reductant over ZrO₂[4-9], Rh/TiO₂[10, 11], MgO[12, 13], and Ga₂O₃[14]. With the exception of Rh/TiO₂, these solid materials exhibit the properties of solid base catalysts; therefore, CO₂ can be adsorbed on the surface of these materials. We have insisted on the importance of CO₂ adsorption on the surface because this makes CO₂, which is a stable and linear molecular, into an active species which provides abundant reactivity for the photocatalytic reduction of CO₂. As mentioned above, it was reported that the photocatalytic reduction CO₂ in the presence of H₂ proceeds over many simple oxides such as ZrO₂, MgO, and Ga₂O₃. 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 Davis-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 ATaO₃ (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 CO₂ was saturated when equilibrium pressure is more than 0.96 kPa. The subtraction between panels a and b was 0.75 μmol·g⁻¹. The equilibrium pressure was about 2.7 kPa when 150 μmol of CO₂ was admitted to the reactor with 2.0 g of LiTaO₃ after the pretreatment. Thus, the amount of CO₂ physisorbed and chemisorbed on LiTaO₃ corresponds to 2.76 and 1.50 μmol under the reaction condition, respectively. Figure 7 demonstrates the amount of chemisorbed CO₂ on ATaO₃ (A = Li, Na, K). Amount of evolved CO gas almost depends on amount of chemisorbed CO₂ in the case of ATaO₃ (A = Li, Na, K) as well as the other reported materials such as ZrO₂, MgO, and Ga₂O₃.

We have reported that MgO exhibits the best photocatalytic activity for the reduction of CO₂ in the presence of H₂ as a reductant under UV light irradiation. It is clarified that the photoactive site of MgO is compatible with the CO₂ adsorption site. The amount of evolved CO gas over MgO (12.9 μmol·g⁻¹) is thirty-first higher than that over LiTaO₃ (0.42 μmol·g⁻¹) under 24 h of photoirradiation using the same light source. On the other hand, amount of chemisorbed CO₂ gas over MgO (130 μmol·g⁻¹) is enormous as compared to that on LiTaO₃ (0.75 μmol·g⁻¹)[12, 13]. Accordingly, the photoactive site of LiTaO₃ would be able to reduce adsorbed CO₂ to CO under photoirradiation effectively. We speculate that a smooth charge separation in LiTaO₃ contributes to the effective photocatalytic reduction of CO₂ in the presence of H₂. 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 LiTaO₃ despite decreasing the specific surface area as shown in Figure 8. The BET specific surface area of LiTaO₃ 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.

Acknowledgement

This study was partially supported by the Program for Improvement of Research

Environment for Young Researchers from Special Coordination Funds for Promoting Science and Technology (SCF), commissioned by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and a Grant-in-Aid for Young Scientists (B), 19760542, 2007, from the Japan Society for the Promotion of Science (JSPS).

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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.

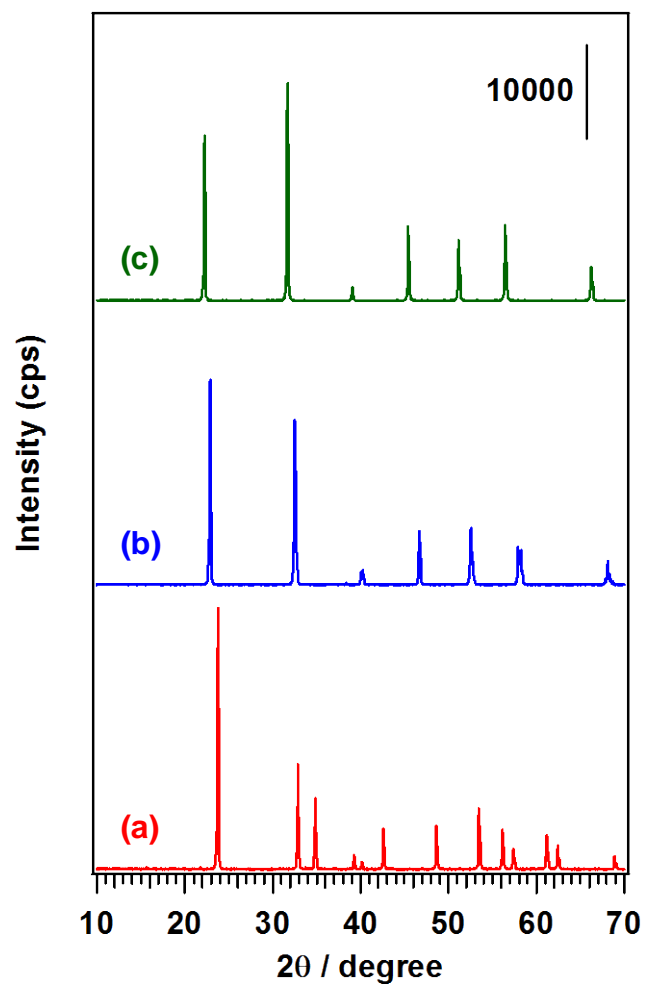


Figure 1

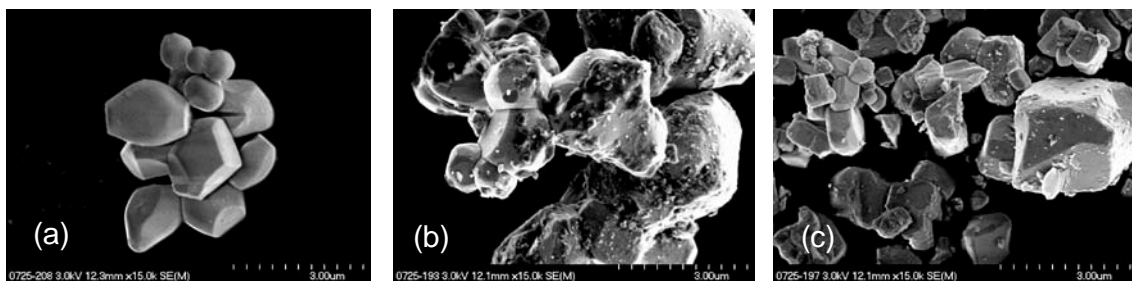


Figure 2

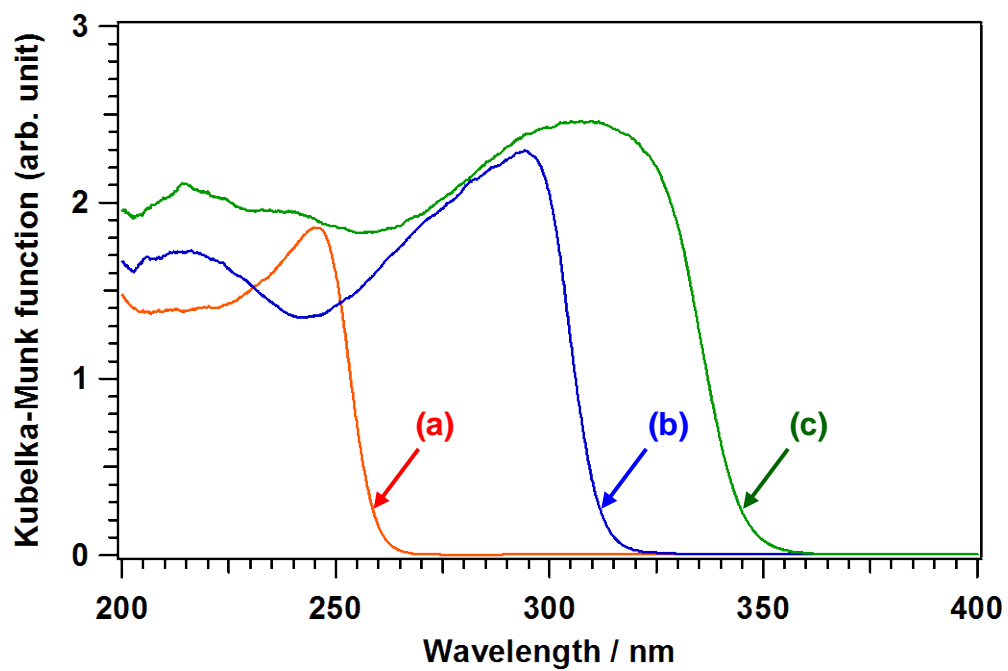


Figure 3

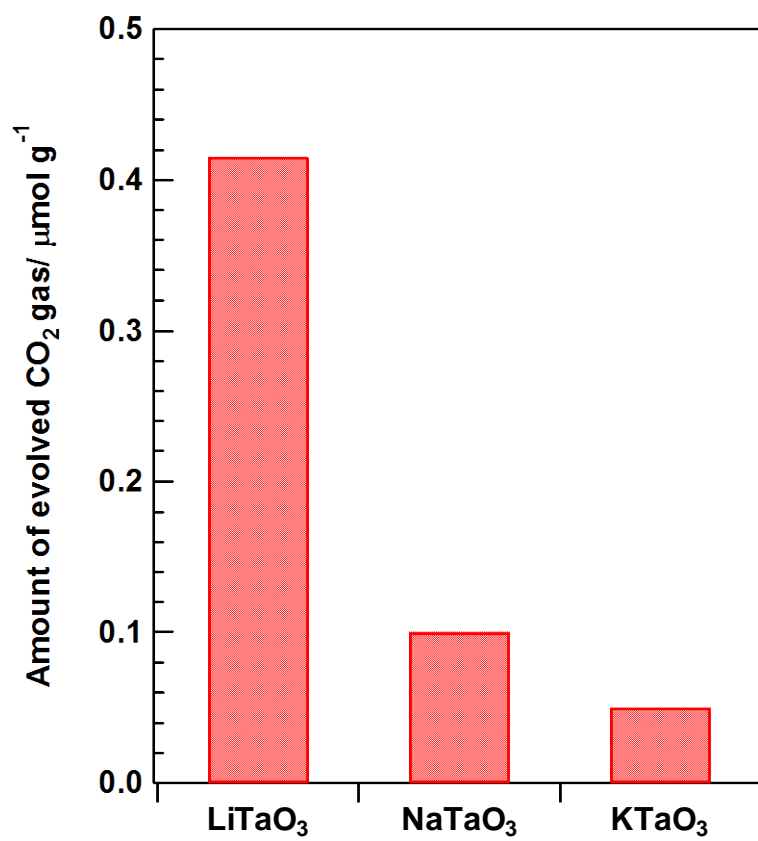


Figure 4

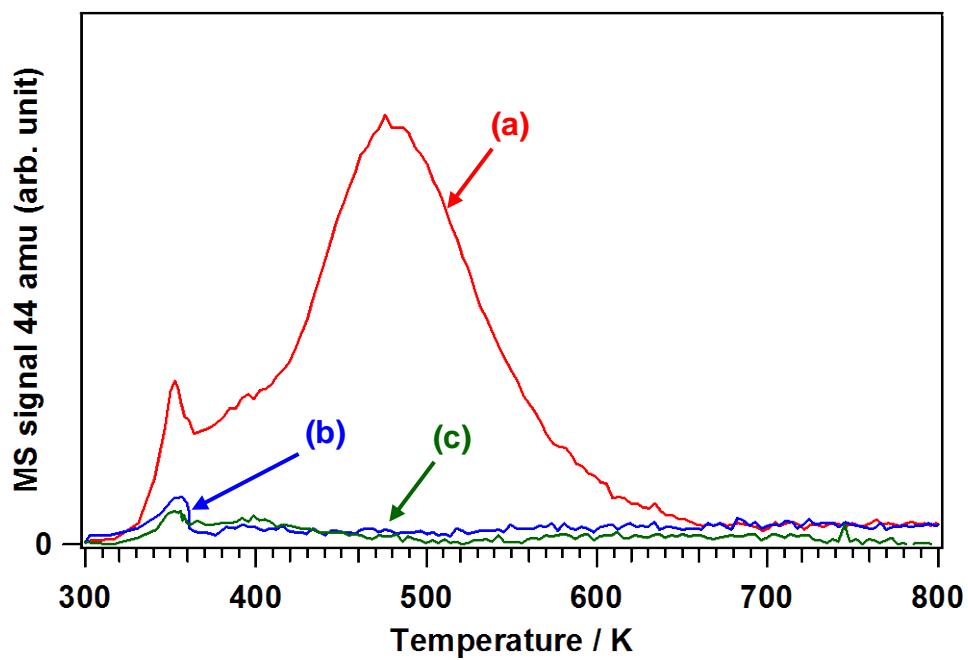


Figure 5

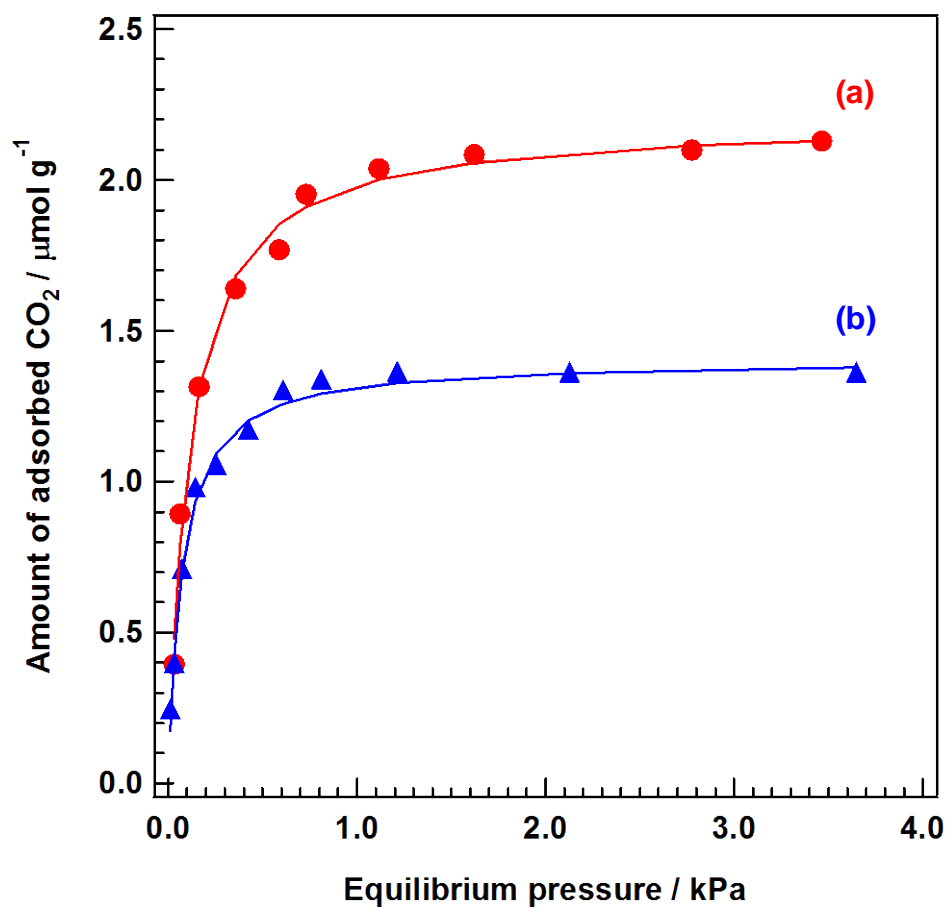


Figure 6

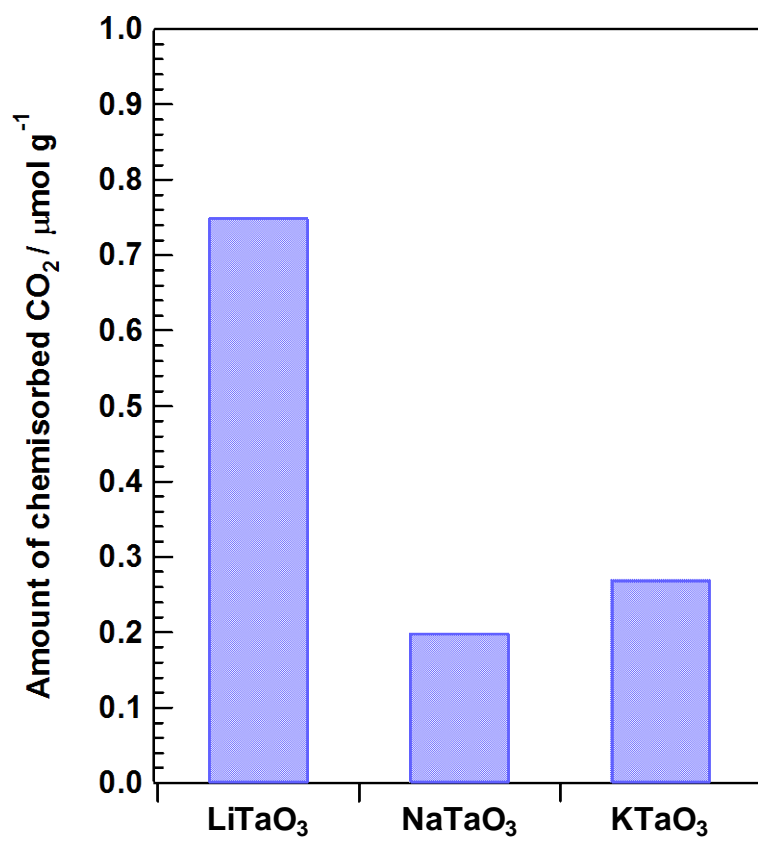


Figure 7

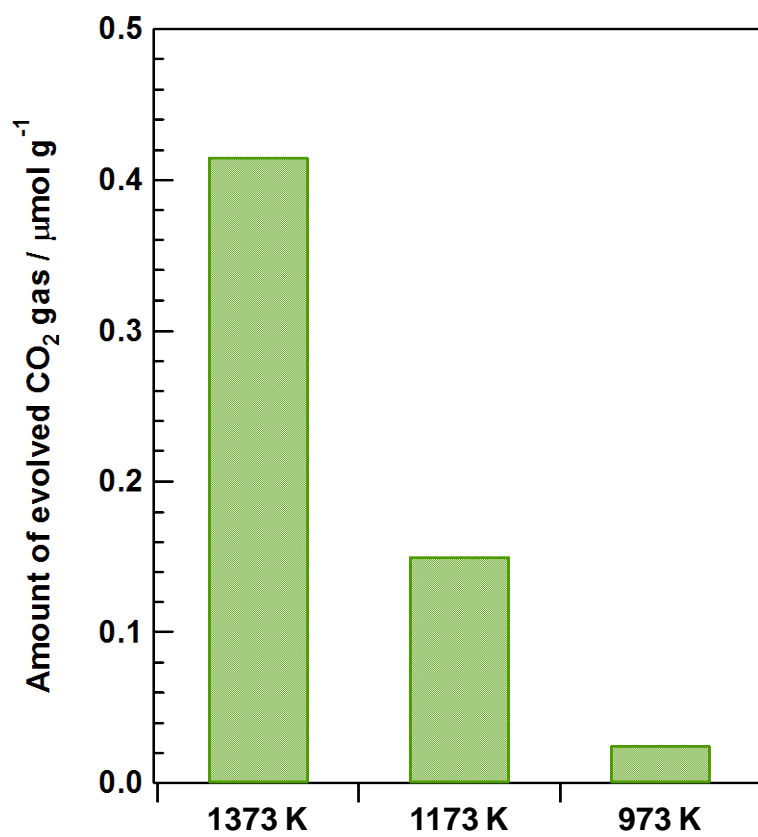


Figure 8