



## Flux method fabrication of potassium rare-earth tantalates for CO<sub>2</sub> photoreduction using H<sub>2</sub>O as an electron donor

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### ABSTRACT

A facile one-pot flux method was applied to fabricate K<sub>2</sub>RETa<sub>5</sub>O<sub>15</sub> (RE = rare-earth element) with tetragonal tungsten bronze (TTB) structures. Pure TTB structures of K<sub>2</sub>RETa<sub>5</sub>O<sub>15</sub> (RE = La, Ce, Pr, Nd, and Sm) with rod-like morphologies were obtained using KCl as the potassium source and flux. For other potassium rare-earth tantalates, the TTB structure was dominant, with an additional RETaO<sub>4</sub> phase present. Among all these K<sub>2</sub>RETa<sub>5</sub>O<sub>15</sub>, K<sub>2</sub>YTa<sub>5</sub>O<sub>15</sub> gave the highest activity for photoreduction of CO<sub>2</sub> with good selectivity toward CO evolution using H<sub>2</sub>O as an electron donor, even in the presence of additional YTaO<sub>4</sub> phase. YTaO<sub>4</sub> fabricated using the flux method under same condition was inactive for photoreduction of CO<sub>2</sub> using H<sub>2</sub>O. It was found that the activity for the photoreduction of CO<sub>2</sub> to be significantly affected by the weight ratio of potassium chloride to yttrium oxide and tantalum oxide (K/YT) in the fabrication process. The highest photoreduction activity achieved in CO evolution was 91.9 μmol h<sup>-1</sup> (for 1.0-g catalyst), with CO selectivity of 84.9%, at K/YT = 1.0. Surface analysis of these tantalates fabricated with different K/YT ratios showed that a high ratio of surface yttrium to tantalum (Y/Ta) was important to achieve a high CO evolution rate.

### 1. Introduction

The energy crisis caused by the consumption of large quantities of fossil fuels, which are non-renewable resources, is considered one of the most important current global issues [1]. Carbon dioxide (CO<sub>2</sub>) emissions from burning fossil fuels have made a significant contribution to global warming because CO<sub>2</sub> is a major greenhouse gas [2]. The conversion of CO<sub>2</sub> to fuels and chemical feedstocks is thought to be an efficient way to solve both the energy crisis and global warming [3,4]. A promising method for CO<sub>2</sub> conversion is the use of renewable energy, such as solar energy, to convert CO<sub>2</sub> into other carbon sources with high energy densities. Heterogeneous photocatalysts have received much attention in CO<sub>2</sub> conversion because they can use solar light directly and be easily to recovery [5,6]. Products such as carbon monoxide (CO) [7], formic acid (HCOOH) [8], formaldehyde (HCHO) [9], methanol (CH<sub>3</sub>OH) [10,11], and methane (CH<sub>4</sub>) [12,13] have been reported from the heterogeneous photoreduction of CO<sub>2</sub>.

Until now, many types of catalysts have been used for the photoreduction of CO<sub>2</sub> [14–16]. However, the activities of these catalysts are often limited by insufficient reduction potentials, high recombination rates of photogenerated electron–hole pairs, and/or poor CO<sub>2</sub> adsorp-

tion capacities. Reaction rates for the reduction products of CO<sub>2</sub> are very low, at usually a few μmol h<sup>-1</sup>. In such cases, it is important to confirm that the carbon-containing products are derived from CO<sub>2</sub> rather than residual carbon contaminants [13,14,17,18]. Therefore, the development of highly efficient catalysts for the conversion of CO<sub>2</sub> is still a great challenge. Recently, our group reported several catalysts with good actives and high selectivity toward CO evolution using H<sub>2</sub>O as an electron donor [19–22]. Isotopic experiments using <sup>13</sup>CO<sub>2</sub>, and/or blank tests, confirmed that the CO product was derived from the conversion of CO<sub>2</sub>. Stoichiometric amounts of O<sub>2</sub> evolution were also detected to ensure that water had been consumed as an electron donor.

Rare-earth element-based catalysts have shown great advantages in solar energy conversion in the last few decades [23–25]. For instance, La-doped NaTaO<sub>3</sub> modified with NiO showed the highest apparent quantum yield at 270 nm for overall water splitting, due to the formation of unique characteristic steps on the surface of the nanostructures [26], which might be beneficial for the separation of photo-generated electrons and holes. K<sub>2</sub>LnTa<sub>5</sub>O<sub>15</sub> (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, and Tm), fabricated using a solid-state reaction (SSR) method, reportedly showed activity in overall water splitting; among these, K<sub>2</sub>SmTa<sub>5</sub>O<sub>15</sub> showed the highest activity using 0.5 wt% NiO cocatalyst

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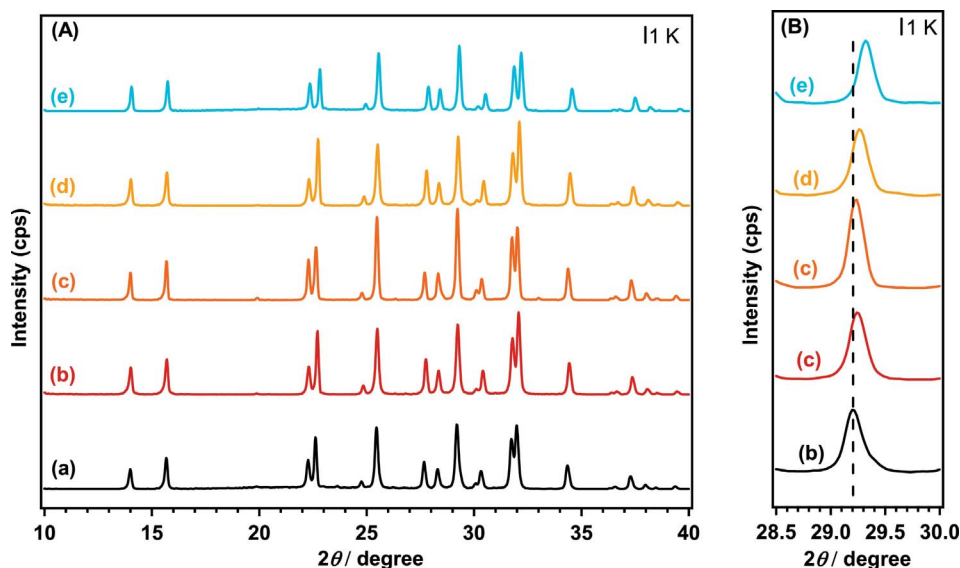


Fig. 1. (A) XRD patterns and (B) the enlarged areas at  $2\theta$  ranged from  $28.5^\circ$  to  $30^\circ$  of  $K_2LaTa_5O_{15}$  (a),  $K_2CeTa_5O_{15}$  (b),  $K_2PrTa_5O_{15}$  (c),  $K_2NdTa_5O_{15}$  (d), and  $K_2SmTa_5O_{15}$  (e), respectively.

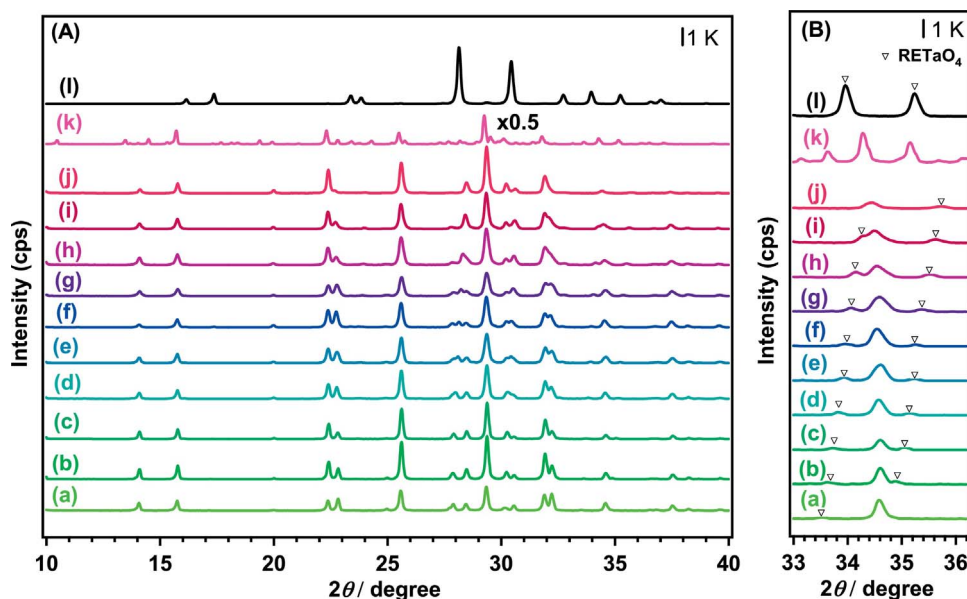


Fig. 2. (A) XRD patterns and (B) the enlarged areas at  $2\theta$  ranged from  $33^\circ$  to  $36^\circ$  of  $K_2EuTa_5O_{15}$  (a),  $K_2GdTa_5O_{15}$  (b),  $K_2TbTa_5O_{15}$  (c),  $K_2DyTa_5O_{15}$  (d),  $K_2HoTa_5O_{15}$  (e),  $K_2YTa_5O_{15}$  (f),  $K_2ErTa_5O_{15}$  (g),  $K_2TmTa_5O_{15}$  (h),  $K_2YbTa_5O_{15}$  (i),  $K_2LuTa_5O_{15}$  (j),  $K_2ScTa_5O_{15}$  (k), and  $YTaO_4$  (l), respectively.

[27]. We recently successfully applied a modified flux method to the fabrication of  $Sr_2KTa_5O_{15}$  with a TTB structure, which showed good activity in the photoreduction of  $CO_2$  to  $CO$  using  $H_2O$  as an electron donor [28]. The TTB structure is perovskite-derived structure, it contains three types of cation tunnels (pentagonal, square, and triangular tunnel), compared with only one type of tunnel (square) in the perovskite structure [29,30]. The materials formed with these three types of tunnels showed a wide variety of occupation possibilities, leading to numerous unique properties [31–33], such as electro-optic ferroelectric [34] and pyroelectric [35] properties. For  $Sr_2KTa_5O_{15}$ ,  $K^+$  and  $Sr^{2+}$  cations occupied the pentagonal and square tunnels, while, similarly,  $K^+$  and  $RE^{3+}$  ( $RE$  = rare-earth element) cations occupied the pentagonal and square tunnels in  $K_2RETa_5O_{15}$  [36]. Therefore, we believe that the flux method could also be applied to the fabrication of  $K_2RETa_5O_{15}$ . To our knowledge, the flux method fabrication of  $K_2RETa_5O_{15}$  and their activities of  $CO_2$  using  $H_2O$  as an electron donor have not reported. In this work, we applied a flux method to fabricate  $K_2RETa_5O_{15}$  with TTB structures, which achieved significant activities for  $CO$  evolution in the photoreduction of  $CO_2$  to  $CO$  using  $H_2O$  as an

electron donor.

## 2. Experimental section

### 2.1. Fabrication of $K_2RETa_5O_{15}$ and deposition of silver

$K_2RETa_5O_{15}$  were fabricated using a flux method with  $KCl$  (99.8%, Wako) as the potassium source and flux. A stoichiometric mixture of  $RE_2O_3$  ( $RE$  = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Tm, Lu, and Sc),  $CeO_2$ ,  $Pr_6O_{11}$ , or  $Tb_4O_7$  (99.9%, Kento), and  $Ta_2O_5$  (99.9%, Kojundo), was ground with  $KCl$  in an  $Al_2O_3$  mortar for 5 min. Unless otherwise noted, the total weight ratio of  $KCl$  salt to rare-earth element oxide and  $Ta_2O_5$  was fixed at 1.0. The above-mentioned mixture was then transferred to a 30-mL  $Al_2O_3$  crucible. The resulting mixture was calcined at 1423 K for 6 h in air. After cooling to room temperature, the mixture was thoroughly washed with distilled water at 358 K three times in order to remove residual salts, and then dried in air at 353 K. The same procedure was employed in all catalyst fabrication processes. For  $K_2YTa_5O_{15}$  fabricated using a different weight ratio of  $KCl$  to  $Y_2O_3$

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