Fast Oxygen Ion Migration in Cu–In–oxide Bulk and Its Utilization for Effective CO2 Conversion at Lower Temperature

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Efficient activation of CO$_2$ at low temperature was achieved by reverse water–gas shift via chemical looping (RWGS-CL) by virtue of fast oxygen ion migration in Cu–In–structured oxide, even at lower temperatures. Results show that novel Cu–In$_2$O$_3$ structured oxide can show a remarkably higher CO$_2$ splitting rate than ever reported. Various analyses revealed that RWGS-CL on Cu–In$_2$O$_3$ is derived from redox between Cu–In$_2$O$_3$ and Cu$_x$In$_y$ alloy. Key factors for high CO$_2$ splitting were fast migration of oxide ions in alloy and the preferential oxidation of the interface of alloy–In$_2$O$_3$ in the bulk of the particles. The findings reported herein can open up new avenues to achieve effective CO$_2$ conversion at lower temperatures.

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Fast oxygen ion migration in Cu–In–oxide bulk and its utilization for effective CO₂ conversion at lower temperature

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Efficient activation of CO₂ at low temperature was achieved by reverse water–gas shift via chemical looping (RWGS-CL) by virtue of fast oxygen ion migration in Cu–In–structured oxide, even at lower temperatures. Results show that novel Cu–In₃O₅ structured oxide can show a remarkably higher CO₂ splitting rate than ever reported. Various analyses revealed that RWGS-CL on Cu–In₃O₅ is derived from redox between Cu–In₃O₅ and Cu-In alloy. Key factors for high CO₂ splitting were fast migration of oxide ions in alloy and the preferential oxidation of the interface of alloy–In₃O₅ in the bulk of the particles. The findings reported herein can open up new avenues to achieve effective CO₂ conversion at lower temperatures.

Anthropogenic emissions of greenhouse gases (GHGs) are regarded as a cause of global warming, which is expected to lead to severe future climate change. Particularly, carbon dioxide (CO₂) derived from fossil fuels and industrial processes has long presented strong effects that continue to raise global mean temperatures. Therefore, development of CO₂ capture and utilization (CCU) technologies represents an urgent task for reducing CO₂ emissions into the atmosphere and for establishing a sustainable carbon cycle. Synthesis of fuels using electricity generation from renewable resources and using CO₂ most notably sun-to-fuel (STF) and power-to-liquids processes, has been proposed as a means of developing CCU. In fact, CO₂-based fuels are anticipated as a technology that can increasingly incorporate renewable energy into the mobility sector as an “e-fuel”. For these fuel production technologies, the potential process route is a Fischer–Tropsch (FT) process using syngas, which includes hydrogen and carbon monoxide (CO) converted from captured CO₂. As a method of efficient conversion of CO₂ to CO through this process, reverse water–gas shift (RWGS) is a promising reaction that uses renewable H₂.

Mallapragada et al. proposed that the STF route consisting of RWGS followed by the FT reaction has higher efficiency than that of other routes with direct CO₂ conversion by photosynthetic bacteria and biomass conversion. The RWGS is an equilibrium limited reaction (equation 1) with an endothermic nature.

\[ \text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H^\circ_{298} = +42.1 \text{ kJ mol}^{-1} \] (1)

This reaction requires high reaction temperatures, separation of gas products to gain high conversion, and a suitable H₂/CO ratio syngas. Furthermore, conventional catalytic RWGS processes include side reactions, as presented in the following equations 2 and 3.

\[ \text{CO} + 3 \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H^\circ_{298} = -206.5 \text{ kJ mol}^{-1} \] (2)
\[ \text{CO} + 4 \text{H}_2 \leftrightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad \Delta H^\circ_{298} = -165.0 \text{ kJ mol}^{-1} \] (3)

The CH₄ produced via these side reactions makes gas separation more complex. Additionally, it loses energy because of the exothermic reaction. One solution for this shortcoming is using chemical-looping reverse water–gas shift (RWGS-CL). The overall concept of solar-driven fuel (chemical) synthesis process with RWGS-CL is presented in Fig. 1. Through this process, CO₂ is converted to CO in two separate steps: reduction and re-oxidation of a metal oxide as an oxygen storage material (OSM). First, OSM is reduced by H₂ (reaction 4). Subsequently, the reduced OSM is re-oxidized by CO₂ to generate pure CO (reaction 5).

\[ \text{CH}_4 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 3 \text{H}_2 \] (4)
\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \] (5)

**Fig. 1.** Concept of solar-driven fuels and chemicals synthesis processes with RWGS-CL.

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MO$_2$ + $\delta$H$_2$ $\rightarrow$ MO$_2$-$\delta$ + $\delta$H$_2$O \hspace{1cm} (4)

MO$_2$-$\delta$ + $\delta$CO$_2$ $\rightarrow$ MO$_2$ + $\delta$CO \hspace{1cm} (5)

Actually, RWGS-CL has benefits deriving from the absence of undesirable side reactions, which drives the equilibrium to CO production, and simplified gas separation, which leads to its improved energy efficiency. In fact, Wenzel et al. investigated solar-to-syngas efficiency for RWGS-CL processes and reported that the energy demand for separation is reduced by 77% compared to conventional RWGS processes \cite{12}. In the RWGS-CL process, the development of OSM is an indispensable factor to make this process feasible. The rates of reduction and oxidation, CO yield, and stability are emphasized as key factors affecting OSM for the RWGS-CL cycles. Furthermore, the operation temperature is an important factor. Isothermal operation at lower temperatures is desired to reduce heat loss and to increase its feasibility \cite{13}. In recent years, great effort has been put forth for the development of OSMs with high redox property for RWGS-CL \cite{13,14,15,16}. This study has revealed that indium-based oxide can be a novel OSM material able to exhibit extremely high isothermal RWGS-CL performance at low temperatures (673–773 K). Particularly, the performance of Cu-modified In$_2$O$_3$ formed from Cu$_2$In$_2$O$_5$ as a parent material was found to be promising for this purpose. Characterizations of OSMs were conducted using powder X-ray diffraction (XRD), a field emission transmission electron microscope equipped with an energy-dispersive X-ray spectrometer (STEM-EDX), X-ray photoelectron spectroscopy (XPS), and in-situ X-ray absorption fine structure (XAFS) measurements.

Fig. 2. Average CO$_2$ splitting rates on Cu-In mixed oxide (this study) and on various oxides in earlier reports.

**Isothermal RWGS-CL performance**

After applying various oxides for RWGS-CL, we found that Cu–In–mixed oxide has high potential for this RWGS-CL. The CO$_2$ splitting performance obtained in this study is presented in Fig. 2 and Table S1 along with results described in earlier reports of the literature. Compared to other perovskite-type oxides \cite{13,14} and ferrite \cite{15,16}, which were reported earlier, Cu$_2$In$_2$O$_5$ showed higher CO$_2$ splitting amounts and rates even at low temperatures such as 673–773 K. Among all the oxides, Cu–In$_2$O$_3$ derived from Cu$_2$In$_2$O$_5$ is the most promising material for low-temperature isothermal RWGS-CL. The cycle performance of isothermal RWGS-CL on Cu$_2$In$_2$O$_5$ at 773 K is presented in ESI Fig. S1. The reduction and oxidation (redox) amounts are defined as the moles of oxygen released or restored per gram of Cu$_2$In$_2$O$_5$. At the first cycle, Cu$_2$In$_2$O$_5$ showed reduction of

Fig. 3. Structural characterization for Cu–In$_2$O$_3$ derived from Cu$_2$In$_2$O$_5$ during each step of the RWGS-CL cycle. (A) XRD diffraction patterns of Cu$_2$In$_2$O$_5$ as prepared, after reduction, and after oxidation. (B) Main diffraction peaks for Cu$_2$In$_2$ alloy on the sample after reduction. EDX image of Cu–In$_2$O$_3$ after reduction (C) and re-oxidation (D) at 773 K (copper, red; indium, green; oxygen, blue). Cu and In K-edge XANES spectra of Cu–In$_2$O$_3$ during the reduction (E) and the re-oxidation (F).
9.50 mmol g⁻¹ and re-oxidation of 4.82 mmol g⁻¹. Then, at cycles 2–5, the reduction and the oxidation amounts were, respectively, 5.06 ± 0.41 mmol g⁻¹ and 4.80 ± 0.40 mmol g⁻¹. Excess reduction at the first cycle (≈ 4.68 mmol g⁻¹) was almost equivalent to the release of 2 mol oxygen atoms per mol of Cu₂In₂O₅. This finding suggests that Cu₂In₂O₅ has become Cu(0)–In₃O₅, which is confirmed later. Products of RWGS-CL were measured using a quadrupole mass spectrometer. The mass spectra of products are presented in ESI Fig. S2. The products at reduction and oxidation steps were identified respectively as H₂O (m/z = 18) and CO (m/z = 28) without production of other by-products. Results confirmed that RWGS-CL on Cu–In₂O₃ formed from Cu₂In₂O₅ is a selective CO₂ conversion to CO.

Structural characterization for this material was achieved using powder XRD, STEM-EDX, and in-situ XAFS measurements. The XRD patterns obtained from fresh and post-reaction samples are portrayed in Fig. 3A. The XRD pattern of the fresh sample showed the formation of Cu₂In₂O₅ with no impurity phase. The XRD pattern of the reduced sample exhibited diffraction peaks assigned to CuIn alloy and In₂O₃. The main compositions of the alloy were Cu₂In₃ and Cu₃In₇ (Fig. 3B). Then, after the oxidation step, diffraction peaks of CuIn alloy disappeared. Those of Cu metal and In₂O₃ were observed. STEM-EDX images are presented in Figs. 3C, D and ESI Fig. S3. The SEM micrographs taken of the reduced Cu–In₂O₃ (ESI Fig. S3A) show the presence of ca. 1 μm particles. The elemental composition of the particles was identified using EDX mapping (copper, red; indium, green; oxygen, blue). Results of EDX mapping of the sample after reduction (Fig. 3C and ESI Fig. S3A) show that indium is distributed evenly over the particle, whereas copper is localized; oxygen is scattered. These images indicate CuIn alloy formation by reduction. For the re-oxidized sample, many particles with uniformly distributed copper, indium, and oxygen were observed as depicted in Fig. 3D and ESI Fig. S5B. Using image processing and analysis for these EDX images with Python (see ESI text and Fig. S4 for details), it was estimated that 84% of In exists as overlapping with Cu, and that 93% of Cu exists as overlapping with In. These results demonstrate that the fine matrix of Cu–In–O was formed in the re-oxidized particle. The Cu in re-oxidized particles was regarded as highly distributed on the surface, or incorporated into the In₂O₃ structure. As additional information, in-situ XAFS results are presented in Figs. 3E and 3F (see ESI text and Figs. S5~S7 for details). The sequential change of In K-edge XANES spectra indicates that the redox of In(III) ⇌ In(0) occurs during the RWGS-CL cycle. By contrast, Cu K-edge XANES spectrum, which only slightly changed during the RWGS-CL cycle, represented the formation of Cu–In alloy. ¹⁷,¹⁸ This structural information obtained from XRD, STEM-EDX, and XAFS measurements demonstrates that the RWGS-CL cycle on Cu₂In₂O₅ as a parent material, is based on the redox of indium with the formation and oxidation of CuIn alloy. This material during RWGS-CL is designated hereinafter as Cu–In₂O₃.

To elucidate the role of Cu in Cu–In₂O₃, we compared the performance of isothermal RWGS-CL as a function of temperature on Cu–In₂O₃ (derived from Cu₂In₂O₅), 10wt% Cu supported on In₂O₃ (10wt% Cu/In₂O₃) and pure In₂O₃ without Cu, as portrayed in Fig. 4. Results indicate that Cu–In₂O₃ is feasible for conducting RWGS-CL, even at 673 K. The performance at each temperature was much higher than that of 10wt% Cu/In₂O₃ and pure In₂O₃ without Cu. Actually, the amount of redox on 10wt% Cu/In₂O₃ was slightly higher than that of In₂O₃, although the CO₂ splitting rate was improved only slightly. Results of structural characterization for 10wt% Cu/In₂O₃ (ESI text and Figs. S8–S11 provide additional details) show that, because of the poor contact of Cu species with In₂O₃ surface, 10wt% Cu/In₂O₃ showed lower performance than that of Cu–In₂O₃ derived from Cu₂In₂O₅.

**Kinetic investigations of oxides during the RWGS-CL cycle**

**Reduction step by H₂.** Temperature-programmed reduction by H₂ (H₂-TPR) measurements, the results of which are presented in Fig. 5A, was done to investigate the reducibility of oxides. The ESI presents additional details.

**Fig. 4 Dependence of RWGS-CL performance of each oxide on the reaction temperature.** Amounts of reduct and average CO₂ splitting during re-oxidation step on Cu–In₂O₃ (A), 10wt% Cu/In₂O₃ (B), and In₂O₃ (C). Reduction was conducted in 10% H₂ atmosphere for 30 min; oxidation was conducted in 10% CO₂ atmosphere.

**Fig. 5. Kinetic analysis for each oxide at the reduction step.** (A) H₂-TPR profiles for Cu–In₂O₃ (derived from Cu₂In₂O₅), 10wt% Cu/In₂O₃ and In₂O₃. (B) Arrhenius plots for the reduction of Cu–In₂O₃ (derived from Cu₂In₂O₅), 10wt% Cu/In₂O₃ and In₂O₃.

For Cu-containing oxides (Cu–In₂O₃ and 10 wt% Cu/In₂O₃), the H₂-TPR profiles showed three notable reduction areas (ca. 400–550 K, 580–700 K, and 700–920 K). In the moderate temperature region of 580–700 K, the amount of reduction was...
equivalent to about 26% of oxygen contained in Cu2In2O5. Therefore, the reduction of In(III) with the formation of Cu-In alloy, the composition of which finally approached Cu9In4, was regarded as proceeding in this moderate temperature region. Regarding results of H2-TPR measurements, results show that Cu species promote the reduction of indium oxide at low temperatures. To investigate more details of the mechanism, the kinetic model for the reduction of these oxides was verified using the method presented by Hancock and Sharp for the isothermal solid-state reaction 10–21. The ESI text, Figs. S12–S15 and Tables S4–S6 present additional details. Kinetic models used for model fitting are shown in ESI Table S3. As a result of the investigations, the phase-boundary-controlled reaction models (R2 and R3 model) were found to be suitable to describe experimentally obtained data for all the oxides. These models are categorized to a classic shrinking core model in which the rate-controlling step is the surface chemical reaction 20,21. The activation energy was investigated using the reaction rate constant k values obtained from the model fitting described above (ESI Table S7). Plots of ln (k) vs. 1/ T (Arrhenius plot) for the three oxides are presented in Fig. 5B. The respective activation energies for Cu–In2O3 (45.2 kJ mol−1) and 10 wt% Cu/In2O3 (53.4 kJ mol−1) were much lower than that for In2O3 (76.6 kJ mol−1), confirming that the Cu species supported on In2O3 decreased the activation barrier for reactions between the surfaces of In2O3 and H2. The slight difference in the activation energy between Cu–In2O3 and 10 wt% Cu/In2O3 suggests that the effect of the Cu species on the reduction does not depend much on these morphologies.

Oxidation step by CO2 for CO formation. Next, kinetic investigations were conducted of the oxidation step by CO2 in the RWGS-CL cycle. The kinetic model for the oxidation of the oxide was also verified using the Hancock and Sharp method. As a consequence of the model fitting (details of which are presented in ESI Figs. S16–S19 and Tables S8–S10), the most suitable models were concluded to be a Zero-order model (R1 model) 19–21 for Cu–In2O3 and the nucleation model, known as the Avraimi–Erofeev model (AE1 model), for the other two oxides 22–24. Figure 6A presents the Arrhenius plot for the oxidation of these three oxides. The reaction rate constant k values obtained from model fitting are presented in Table S11. The activation energy for Cu–In2O3 is 50.7 kJ mol−1, which is markedly lower than that for either of the other two oxides. As results of the model fitting show, the large difference in the activation energy is attributable to the different mechanisms of oxidation among these oxides. Considering that AE1 is suitable as a model for In2O3 and 10 wt% Cu/In2O3, results show that the overall oxidation of these two oxides is determined by the rate of formation and growth of the indium oxide nuclei. At the beginning of the reaction, the rate of oxidation is high because of random nucleation on the surface of the reduced oxide. However, as the nucleation and nuclei growth proceed, the rate of oxidation plummets because of the decrease of the reduced surface. As a result, a long time is necessary to complete oxidation by CO2.

Figure 6B presents different rates of CO2 splitting over these oxides during oxidation by CO2. For all oxides, the degree of reduction before re-oxidation was fixed at 3.0 mmol g−1. On In2O3 and 10 wt% Cu/In2O3, the CO2 splitting rate decreased drastically with the progress of oxidation. The oxidation of Cu–In2O3 proceeded while maintaining a constant CO2 splitting rate of about 340 μmol g−1 min−1 until conversion reached 60%. As a result, re-oxidation of the reduced Cu–In2O3 is completed twice as rapidly as those of the other two oxides. These results obtained from the kinetic investigation for Cu–In2O3 suggest that the amount of the active site for CO2 splitting remains constant while oxidation is proceeding. Figure 6C shows the surface In/O ratio at each oxidation rate of the reduced Cu–In2O3 and 10wt% Cu/In2O3, as measured by XPS. The In/O ratio of the Cu–In2O3 surface remained above 0.9, even at the oxidation rate of 75%, which indicates that bulk oxidation proceeds preferentially while the surface remains in a highly reduced state. This particular CO2 splitting mechanism of Cu–In2O3 is explainable as shown in Figure 6D. First, CO2 splits on the surface of Cu–In alloy; the CO and oxide ion (O2−) are generated. Subsequently, the O2− migrates to the bulk of the particle. It presumably oxidizes the Cu–In alloy–In2O3 interface. As a result, the alloy surface, as the active site, remains in a highly reduced state. Rapid CO2 splitting proceeds continuously.

Conclusion
As reported herein, Cu–In2O3 was synthesized. Then its performance for RWGS-CL was investigated at the low
temperatures of 673–773 K. Results of RWGS-CL cycle tests demonstrated that, even at low temperatures, Cu-In$_2$O$_3$ exhibited much higher CO$_2$ splitting performance than ever reported. Results of XRD, STEM-EDX, and in-situ XAFS measurements showed that the oxide has a structure of reduced Cu supported on In$_2$O$_3$ (Cu-In$_2$O$_3$) under the RWGS-CL condition, and showed that its redox property is based on Cu-In$_2$O$_3$ alloy formation and re-oxidation. In addition, because low performance was exhibited by pure In$_2$O$_3$ and Cu supported In$_2$O$_3$ that were prepared using an impregnation method, the structured state of Cu-In$_2$O$_3$ has extremely important roles for its high RWGS-CL performance. H$_2$-TPR and kinetic investigations revealed that Cu-In$_2$O$_3$ shows high reducibility, even at low temperatures. We concluded that Cu species promote the reaction of H$_2$ with the oxide surface. Results of kinetic investigations in the oxidation step indicate that the Cu-In$_2$O$_3$ particle surface conserved a highly reduced state, even in a re-oxidation condition, resulting in rapid completion of re-oxidation by CO$_2$. The interesting oxidation behavior is attributed to rapid O$^{2-}$ migration from the surface to bulk of the Cu-In$_2$O$_3$ alloy and preferential oxidation of the interface of alloy-In$_2$O$_3$. The combination of high reducibility and the specific re-oxidation mechanism engenders the high performance found for RWGS-CL on Cu-In$_2$O$_3$.

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Conflicts of interest

There are no conflicts to declare.

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Materials and Methods

Preparation of oxide powder

Using a complex polymerization method, Cu$_2$In$_2$O$_5$ and In$_2$O$_3$ powders were prepared. For them, Cu(NO$_3$)$_2$·3H$_2$O and In(NO$_3$)$_3$·nH$_2$O (Kanto Chemical Co. Inc.) were used as precursors. After metal nitrates were dissolved in distilled water, excess citric acid and ethylene glycol (Kanto Chemical Co. Inc.) were added to the solution. The molar ratio of metal ion: citric acid: ethylene glycol was 1:3:3. The solution was dried and pre-calcined for 2 h at 673 K. After pre-calcination, the obtained powder was calcined for 10 h at 1123 K.

Using a wet-impregnation method, Cu-loaded In$_2$O$_3$ was prepared. First, In$_2$O$_3$ was soaked in 20 mL of distilled water. Next, it was stirred for 2 h using a rotary evaporator in vacuo at room temperature. Subsequently, Cu(NO$_3$)$_2$·3H$_2$O dissolved in 20 mL distilled water was added to the solution and was stirred again for 2 h under atmospheric pressure. After the solution was dried, the obtained sample powder was calcined at 773 K for 5 h.

Isothermal RWGS-CL cycle test

Isothermal RWGS-CL cycle testing was conducted using a thermogravimetric apparatus (TG-50A; Shimadzu Corp.). First, oxide powder filled in a sample pan was ramped up to pre-set temperatures (673, 723, 773, 823, 873 K) in Ar flow. Then, the oxide powder was reduced by 10 vol% H$_2$ balanced by Ar for 30 min (reduction step). After the reduction step, the reduced oxide was re-oxidized by 10% CO$_2$ (Ar balance) until no increase of the sample weight could be observed. A series of reduction and oxidation steps was defined as one cycle of isothermal RWGS-CL. The total flow rate was set constant to 100 mL min$^{-1}$. The amounts of reduction and oxidation (redox) were defined as the amounts of oxygen atoms released or restored in each step, as calculated using the following equation S1.

$$\text{Amount of reduction or oxidation (redox)[mmol g}^{-1}]=\frac{|\Delta m|}{m_{\text{sample}} \times M_O} \quad (S1)$$

In this equation, $\Delta m / \text{mg}$, $m_{\text{sample}} / \text{g}$ and $M_O / \text{g mol}^{-1}$ respectively represent the change of sample weight during each step, the initial sample weight, and molar mass of oxygen atom. The average CO$_2$ splitting rate was defined as shown in equation S2.

$$\text{Average CO}_2 \text{ splitting rate [\mu mol g}^{-1} \text{ min}^{-1}]=\frac{\text{Amount of oxidation}}{\Delta t} \times 10^3 \quad (S2)$$

Therein, $\Delta t / \text{min}$ represents the time necessary to complete CO$_2$ oxidation. The differential reaction rate was also used for kinetic studies.

Temperature-programmed experiment

Temperature-programmed reduction by H$_2$ (H$_2$-TPR) was conducted using a thermogravimetric apparatus (TG-50A; Shimadzu Corp.) to evaluate the reduction
properties of oxides. Oxide powder was heated from room temperature to 973 K in 10% H₂ flow at a ramping rate of 2 K min⁻¹.

Structural characterization for oxides

Powder X-ray diffraction (XRD) measurements were taken to elucidate the crystal structure of oxides using an X-ray diffractometer (Smart Lab-III; Rigaku Corp.) with Cu-Kα radiation at 40 kV and 40 mA. Observation of the oxide particle morphology and the distribution of elements such as copper, indium, and oxygen were conducted using a scanning transmission electron microscope with an energy-dispersive X-ray spectrometer (STEM-EDX; HE-2200; Hitachi Ltd.). Furthermore, calculation of the overlapping ratio between indium and copper was conducted using EDX images processed by Python. For image processing, each EDX-image of indium and copper was divided into square areas of pixels. Then each area was blurred and binarized. The indium ratio overlapping with Cu was calculated by dividing the copper existence area determined in the binarization by the Indium existence area also determined in the binarization. The copper ratio overlapping with indium was calculated similarly.

In-situ X-ray adsorption fine structure

In-situ X-ray adsorption fine structure (XAFS) analyses for In and Cu K-edge were conducted at the beamline BL07 of the SAGA Light Source. The Cu₂In₄O₉ powder was diluted by boron nitride (BN) and was pressed into a 10 mmϕ pellet. The pellet was attached to a cell for in-situ experiments. First, the sample pellet was ramped up to 523 K in N₂ flow and was pre-reduced by 10% H₂ (N₂ balance) for 60 min at 523 K. The XAFS spectra were measured during pre-reduction. After pre-reduction treatments, the pellet was ramped up to 773 K in N₂ flow. Then reduction by H₂ and oxidation by CO₂ of the pellet was conducted at 773 K. The XAFS spectra were measured in each treatment. The gas compositions were 10% H₂ (N₂ balance) at the reduction step and 10% CO₂ (N₂ balance) at the oxidation step. The total flow rate was set constant to 100 mL min⁻¹ in the experiments. The obtained XAFS spectra were analyzed using software (Athena ver. 0.9.26).

EDX map processing and analysis for Cu-In₂O₃ during RWGS-CL

In order to estimate the Indium ratio overlapping with Copper in the STEM-EDX images, image analysis of EDX maps (Fig. S3B) was conducted after processing the images by python3. In the processing, EDX map images of Copper and Indium were first blurred and binarized as shown in Fig. S4. Blurring and binarizing were conducted with the help of CV2 library in OpenCV. The function used in the blurring is as follows.

blurred_image = cv2.GaussianBlur(image, (5, 5), 0)
Arguments passed to the cv2. GaussianBlur function are the original EDX-mapping image (image), gaussian kernel size (5,5) and the standard deviation of x axis (0 of automation) respectively. The function used in the binarizing is as follows.

\[
\text{threshold, binarized\_image} = \text{cv2.threshold(blurred\_image, 5, 255, cv2.THRESH\_BINARY)}
\]

Arguments passed to the cv2.threshold function are the blurred image (blurred image), threshold (5), binarizing value for the pixel surpassed threshold (255) and the method of binarizing (cv2.THRESH\_BINARY) respectively. And finally, the Indium ratio overlapping with Copper was estimated using the following calculation, with the help of NumPy library represented as np.

\[
\text{In\_ratio} = \frac{\text{np.count\_nonzero(Cu\_binarized\_image==255)}}{\text{np.count\_nonzero(In\_binarized\_image == 255)}}
\]

The Copper ratio overlapping with Indium was estimated in the same way.

In addition, Indium (Copper) ratio overlapping with Copper (Indium) in the STEM-EDX of 10wt\% Cu/In$_2$O$_3$ (Figs. S10 and S11) was estimated in the same manner as Cu-In$_2$O$_3$.

**In-situ XAFS measurements**

To investigate more details of the redox mechanism of Cu-In$_2$O$_3$, in-situ XAFS measurements were conducted. The measurement procedure is shown in the method section. First, the Cu K-edge and In K-edge XANES spectra of Cu-In$_2$O$_3$ during pre-reduction are presented respectively in Figs. S5 and S6. The spectra of Cu K-edge and In K-edge for as-prepared Cu$_2$In$_2$O$_5$ were, respectively, similar to those of CuO and In$_2$O$_3$. The valence of In and Cu in Cu$_2$In$_2$O$_5$ were considered to be In(III) and Cu(II). By pre-reduction, the spectrum of Cu K-edge changed to a similar spectrum to that of Cu-foil, whereas the spectrum of In K-edge changed only slightly. These results demonstrate that only the reduction of Cu(II) in Cu$_2$In$_2$O$_5$ to Cu(0) proceeded. Figure S7 presents XANES spectra of In K-edge (panels A and B) and Cu K-edge (panels C and D) during RWGS-CL cycle at 773 K. The degree of reduction of In during RWGS-CL was estimated using a linear combination fitting (LCF) analysis (Table S2). The reduction of Cu-In$_2$O$_3$ proceeds by 49.3% in 30 min. Moreover, the oxidation was almost completed in 60 min, which agrees well with cycle reaction test results. Characteristic XANES spectra of Cu K-edge were observed during H$_2$ reduction at 773 K. The spectra do not correspond to those of Cu-foil, CuO, and Cu$_2$O as standard samples. They can not be replicated by a linear combination of these standard samples. For the spectra, the peak intensity assigned to the 1s to 4p transition decreased compared to that for the Cu-foil spectrum, which indicates that Cu metallic atoms interact with other metallic atoms. The electron of In atoms was probably transferred to metallic Cu atoms because of the difference of electronegativity between Cu and In. Similar features of XANES spectra were described in earlier reports of bimetallic compounds such as Sn@Cu core–shell nanoparticles $^{17,18}$. The formation of Cu-In alloy was also confirmed from these in-situ XAFS measurements. During the oxidation step, this characteristic
spectrum for Cu only slightly changed for 30 min, which demonstrates that the In oxidation proceeds while most of the Cu retains its interaction with the un-oxidized In, which is consistent with the oxidation mechanism inferred from the reaction model fitting, which mentioned later.

**Structural characterization of 10wt% Cu/In$_2$O$_3$**

The structural information (powder XRD and STEM-EDX) for 10wt% Cu/In$_2$O$_3$ is presented in Figs. S8–S10. As these results show, the RWGS-CL cycle on 10wt% Cu/In$_2$O$_3$ is based on the redox of indium with the formation and re-oxidation of Cu$_x$In$_y$ alloy, as in the case of Cu-In$_2$O$_3$. As a result of the image processing and analysis for these EDX images (Fig. S11), although the 98% of Cu exists overlapping with In, only 57% of In present in the field overlapped with Cu after reduction. This fact indicates that the large Cu particle migrated to the surface of In$_2$O$_3$ during oxidation and ended up losing sufficient contact with In$_2$O$_3$.

**Temperature-programmed reduction by H$_2$ (H$_2$-TPR)**

Temperature-programmed reduction by H$_2$ (H$_2$-TPR) measurements was conducted to investigate the reducibility of oxides (Cu-In$_2$O$_3$, 10wt% Cu/In$_2$O$_3$ and pure In$_2$O$_3$ without Cu loading), the results of which are presented in Fig. 5A. The reduction of In$_2$O$_3$ occurred at temperatures higher than 700 K. This finding agrees with earlier reports of the literature for In$_2$O$_3$ catalysts. In the case of Cu-containing oxides (Cu-In$_2$O$_3$ and 10wt% Cu/In$_2$O$_3$), the H$_2$-TPR profiles showed three notable reduction areas (about 400–550 K, 580–700 K, and 700–920 K). The H$_2$-TPR behavior of Cu-In$_2$O$_3$ from Cu$_2$In$_2$O$_5$ can be represented by the following equations S3–S5.

\[
\text{Cu}_2\text{In}_2\text{O}_5 + 2 \text{H}_2 \rightarrow \text{Cu}_2\text{In}_2\text{O}_3 + 2 \text{H}_2\text{O} \quad \text{(S3)}
\]

\[
\text{Cu}_2\text{In}_2\text{O}_3 + 1.3 \text{H}_2 \rightarrow \text{Cu}_2\text{In}_{0.87}\text{In}_{1.13}\text{O}_{1.7} + 1.3 \text{H}_2\text{O} \quad \text{(S4)}
\]

\[
\text{Cu}_2\text{In}_{0.87}\text{In}_{1.13}\text{O}_{1.7} + 1.7 \text{H}_2 \rightarrow \text{Cu}_2\text{In}_{0.87}\text{In}_{1.13}\text{metal} + 1.7 \text{H}_2 \quad \text{(S5)}
\]

Reduction in the low-temperature region of 400–550 K (equation S3) was the reduction of Cu(II) to Cu(0). In the moderate temperature region of 580–700 K, the amount of reduction was equivalent to about 26% of oxygen contained in Cu$_2$In$_2$O$_5$. Therefore, the reduction of In(III) with the formation of Cu$_x$In$_y$ alloy, the composition of which finally reached near Cu$_3$In$_4$, was considered to proceed in this moderate temperature region (equation S4). Then, the remaining indium oxide was simply reduced in the high-temperature region as shown in equation S5. For 10 wt% Cu/In$_2$O$_3$, the reduction steps are similar to that of Cu-In$_2$O$_3$ because the H$_2$-TPR profile shows three reduction regions.

**Reaction kinetic models**

In order to investigate the mechanism of isothermal solid-state reaction in the RWGS-CL condition, the reaction kinetic study was conducted. In this study, the method
which Hancock and Sharp proposed to distinguish reaction mechanisms\textsuperscript{17}, was applied. The following equation S6 derives from Avrami-Erofe’ev equation\textsuperscript{20–22} which are based on the classical nucleation and grain growth model.

\[
(\dot{i} a) + n \ln \dot{i} = \ln \frac{\dot{i}}{-\ln(1-x)}
\]

\text{(S6)}

where \(x\) is the fraction reacted in time \(t\) (: the solid conversion), \(a\) is the constant based on the frequency of the nuclei formation and the rate of grain growth, and \(n\) is the constant associated with the geometry of the system.

In this method, the plots of \(\ln(-\ln(1-x))\) vs. \(\ln(t)\) is used to infer a suitable model for the reaction focused on. Table S3 shows rate equations and \(n\) values for various solid-state reaction models. Besides the nucleation model, the Phase-boundary-controlled reaction model which is categorized to shrinking core model, reaction order model and the diffusion model are typical reaction models for isothermal solid-phase reactions. Hancock and Sharp proposed that the linear plots are obtained for these models as well, if the conversion \(x\) is limited to the range of 0.15–0.5. Therefore, it is possible to verify the kinetic model by the value of slope \(n\) obtained from the plots, and this method has been employed in previous literatures for Chemical-looping process\textsuperscript{18,19}.

**Model fitting for the reduction of oxides**

In this study, the experimental data of the reduction by \(H_2\) was obtained by a thermogravimetry. The conversion of the reduction is defined as following equation S7.

\[
x(\text{reduction}) = \frac{m_i - m_f}{m_i - m_t}
\]

\text{(S7)}

where \(m_i\) is the initial weight, \(m_t\) is the weight at a time and \(m_f\) is the final weight of oxides. For pure \(In_2O_3\), \(m_t\) is defined as the weight when completely reduced to In metal. On the other hand, for Cu containing oxides (Cu-In\(_2\)O\(_3\) and 10wt\% Cu/In\(_2\)O\(_3\)), \(m_t\) is defined as the weight at the end of Cu-In alloy formation, in order to investigate the kinetic model for the reduction with the formation of Cu-In alloy. Figure S12 presents the plots of \(\ln(-\ln(1-x))\) vs. \(\ln(t)\) for the reduction of oxides by \(H_2\). Since the average \(n\) values were 1.038–1.074, AE1, R2 and R3 models were adopted as the candidates for a suitable model. The experimental and calculated conversion are shown in Figs. S13–S15. The phase-boundary-controlled reaction models (R2 and R3) seemed to fit relatively well to the experimental data. Comparing the experimental data and the calculated conversion, root-mean square deviation (RMSD) was investigated and presented in Tables S4–S6. The models with smaller RMSD value were determined as the suitable model.

**Model fitting for the oxidation of reduced oxides**
In this study, the experimental data for the oxidation by CO\textsubscript{2} was obtained by a thermogravimetry. The conversion of oxidation step is defined as following equation S8.

\[ x(\text{oxidation}) = \frac{m_f - m_t}{m_f - m_i} \]  

(S8)

where \( m_i \) is the initial weight, \( m_t \) is the weight at a time and \( m_f \) is the final weight of oxides. Pre-reduction by H\textsubscript{2} was conducted for all the oxides. For the Cu containing oxides (Cu-In\textsubscript{2}O\textsubscript{3} and 10wt\% Cu/In\textsubscript{2}O\textsubscript{3}), pre-reduction was conducted until the Cu-In alloy formation finished, in order to investigate the kinetic model for the oxidation of Cu-In alloy. Figure S16 presents the plots of ln(−ln(1−\(x\))) vs. ln(\(t\)) for the oxidation of the reduced oxides. Since the average \( n \) values were 0.832–1.218, AE1, R1, R2 and R3 models were adopted as the candidates for a suitable model. The experimental and calculated conversion are shown in Figs. S17–S19. As for Cu-In\textsubscript{2}O\textsubscript{3}, the Zero-order reaction model (R1) shows good fitting, although the gap is bigger between the calculation and the experimental data as the conversion increased higher than 0.7–0.8 (Fig. S17 and table S8). Thus, most of the oxidation proceeds according to the R1 model, and the rate-determining step is considered to be changed in the high conversion region. For other two oxides, the most suitable model is determined as AE1 model (Figs. S18, S19 and tables S9, S10).
Fig. S1.
Isothermal RWGS-CL performance on Cu$_2$In$_2$O$_5$ at 773 K. Bars represent the amount of reduction (blue bars) and oxidation (red bars).
Fig. S2.

H\textsubscript{2}O and CO formation during isothermal RWGS-CL on Cu\texttextsubscript{2}In\textsubscript{2}O\textsubscript{5} at 773 K.
Fig. S3.

STEM-EDX images of Cu-In$_2$O$_3$ after RWGS-CL cycle. STEM-EDX images for Cu$_2$In$_2$O$_5$ (A) after reduction at 773 K and (B) after oxidation at 773 K (copper – red; indium – green; oxygen – blue).
Fig. S4.
Binarized EDX mapping images for Cu-In$_2$O$_3$ after oxidation at 773 K.
Fig. S5.

Cu K-edge XANES spectra for Cu₂In₂O₅ during pre-reduction at 523 K. (A) Sequential change of Cu K-edge XANES spectrum for Cu₂In₂O₅ during pre-reduction at 523 K. (B) The comparison of XANES spectrum for prepared Cu₂In₂O₅ with that for standard samples (CuO, Cu₂O and Cu-foil).
Fig. S6.
In K-edge XANES spectra for Cu$_2$In$_2$O$_5$ during pre-reduction at 523 K. (A) Sequential change of In K-edge XANES spectrum for Cu$_2$In$_2$O$_5$ during pre-reduction at 523 K. (B) The comparison of XANES spectrum for prepared Cu$_2$In$_2$O$_5$ with that for standard samples (In$_2$O$_3$ and In-foil).
Fig. S7.
**XANES spectra for Cu-In$_2$O$_3$ during RWGS-CL cycle at 773 K.** In K-edge XANES spectra of Cu-In$_2$O$_3$ during reduction (A) and re-oxidation (B). Cu K-edge XANES spectra of Cu-In$_2$O$_3$ during reduction (C) and re-oxidation (D).
Fig. S8.
XRD diffraction patterns of 10wt% Cu/In$_2$O$_3$. (A) XRD profiles of 10wt% Cu/In$_2$O$_3$ as prepared, after reduction and after re-oxidation. (B) Main diffraction peaks for Cu$_x$In$_y$ alloy in the XRD profile of 10wt% Cu/In$_2$O$_3$ after reduction.
Fig. S9.
STEM-EDX images for 10wt% Cu/In$_2$O$_3$ after reduction at 773 K.
Fig. S10.
STEM-EDX images for 10wt% Cu/In$_2$O$_3$ after oxidation at 773 K.
Fig. S11.
Binarized EDX mapping images for 10wt%Cu/In$_2$O$_3$ after oxidation at 773 K.
Fig. S12.
Plots of $\ln(-\ln(1-x))$ vs. $\ln(t)$ for the reduction of Cu-In$_2$O$_3$, 10wt% Cu/In$_2$O$_3$ and pure In$_2$O$_3$ by H$_2$. 
Fig. S13.
Comparison of experimental data for reduction of Cu-In$_2$O$_3$ by H$_2$ with Phase-boundary controlled reaction model (R2 and R3).
Fig. S14.
Comparison of experimental data for reduction of 10wt% Cu/In$_2$O$_3$ by H$_2$ with Phase-boundary controlled reaction model (R2 and R3).
Fig. S15.
Comparison of experimental data for reduction of pure $\text{In}_2\text{O}_3$ by $\text{H}_2$ with Avrami-Erofe’ev model (AE1) and Phase-boundary controlled reaction model (R3).
Fig. S16.
Plots of ln(−ln(1−x)) vs. ln(t) for the oxidation of Cu-In$_2$O$_3$, 10wt% Cu/In$_2$O$_3$ and pure In$_2$O$_3$ by CO$_2$. 
Fig. S17.
Comparison of experimental data for oxidation of Cu-In$_2$O$_3$ by CO$_2$ with Avrami-Erofe'ev model (AE1), Zero order reaction model (R1) and Phase-boundary controlled reaction model (R2 and R3).
Fig. S18.
Comparison of experimental data for oxidation of 10wt% Cu/In$_2$O$_3$ by CO$_2$ with Avrami-Erofe’ev model (AE1) and Phase-boundary controlled reaction model (R2 and R3).
Fig. S19.
Comparison of experimental data for pure In$_2$O$_3$ with Avrami-Erofe’ev model Phase-boundary controlled reaction model (R2 and R3).
| Material                  | Oxidation temperature / K | Partial pressure of CO$_2$ / % | CO$_2$ splitting amount / mmol g$^{-1}$ | CO$_2$ splitting rate / mol g$^{-1}$ min$^{-1}$ | Reference |
|---------------------------|---------------------------|-------------------------------|----------------------------------------|-----------------------------------------------|-----------|
| La$_{0.75}$Sr$_{0.25}$FeO$_3$ | 823                       | 6.7                           | 4.00                                   | 73.1                                          | (13)      |
| La$_{0.6}$Ca$_{0.4}$Fe$_{0.4}$Mn$_{0.4}$O$_3$ | 823                       | 10                            | 0.973                                  | 160                                           | (14)      |
| Mn$_{0.2}$Co$_{0.8}$Fe$_2$O$_4$            | 923                       | 20                            | 8.8                                    | 142.3                                         | (15)      |
| Cu$_{0.4}$Co$_{0.6}$Fe$_2$O$_4$            | 823                       | 20                            | -                                      | 98.3                                          | (16)      |
| In$_2$O$_3$                | 673                       | 10                            | 0.46                                   | 17.4                                          |           |
|                           | 723                       | 10                            | 1.11                                   | 37.2                                          | This work |
|                           | 773                       | 10                            | 1.64                                   | 93.4                                          |           |
| 10 wt% Cu/In$_2$O$_3$      | 673                       | 10                            | 0.45                                   | 3.5                                           | This work |
|                           | 723                       | 10                            | 1.60                                   | 28.5                                          |           |
|                           | 773                       | 10                            | 2.79                                   | 117.0                                         |           |
| Cu-In$_2$O$_3$             | 673                       | 10                            | 2.90                                   | 58.7                                          |           |
|                           | 723                       | 10                            | 3.79                                   | 115.0                                         |           |
|                           | 773                       | 10                            | 4.80 $\pm$ 0.40                       | 161.8 (1st cycle)                             | This work |
|                           |                           |                               |                                        | 85.5 (5th cycle)                              |           |

Table S1.
Comparison of the CO$_2$ splitting performance at low temperature range with the various oxides in previous reports.
Table S2.
Ratio of In(0) during the reduction and the oxidation at 773 K, as estimated by linear combination fitting of In K-edge spectra.

| Time / min | Ratio of In (0) during reduction step / % | Ratio of In (0) during oxidation step / % |
|------------|------------------------------------------|------------------------------------------|
| 10         | 28.5                                     | 48.7                                     |
| 20         | 41.8                                     | 33.6                                     |
| 30         | 49.3                                     | 20.4                                     |
| 40         | -                                        | 6.7                                      |
| 50         | -                                        | 2.8                                      |
| 60         | -                                        | 1.9                                      |
Table S3. 
Rate equations and n values for various solid-state reaction models.

| Function | Reaction model                                      | Equation                           | n    |
|----------|----------------------------------------------------|------------------------------------|------|
| D1       | One-dimensional diffusion                         | $x^2 = kt$                         | 0.62 |
| D2       | Two-dimensional diffusion Valensi equation         | $(1-x)\ln(1-x) + x = kt$          | 0.57 |
| D3       | Three-dimensional diffusion Jander equation        | $[1-(1-x)^{1/3}]^2 = kt$          | 0.54 |
| AE1      | Avrami-Erofe’ev (n = 1)                            | $-\ln(1-x) = kt$                  | 1    |
| AE3      | Avrami-Erofe’ev (n = 3)                            | $-\ln(1-x)^{1/3} = kt$            | 3    |
| R1       | Zero order reaction                                | $x = kt$                          | 1.24 |
| R2       | Phase-boundary-controlled reaction (contracting area) | $1-(1-x)^{1/2} = kt$              | 1.11 |
| R3       | Phase-boundary-controlled reaction (contracting volume) | $1-(1-x)^{1/3} = kt$              | 1.07 |
Table S4.
Root-mean square deviation to compare calculation conversion and experimental conversion for the reduction of Cu-In$_2$O$_3$.

| Temperature / K | Root Mean Square Deviation |
|-----------------|----------------------------|
|                 | R3 | R2 |
| 673             | 0.0620 | 0.0076 |
| 723             | 0.0709 | 0.0296 |
| 773             | 0.0406 | 0.0056 |
| 823             | 0.0840 | 0.0406 |
Table S5.
Root-mean square deviation to compare calculation conversion and experimental conversation for the reduction of 10wt% Cu/In$_2$O$_3$.

| Temperature / K | Root Mean Square Deviation |
|-----------------|----------------------------|
|                 | R3  | R2  |
| 723             | 0.0166 | 0.0470 |
| 748             | 0.0132 | 0.0377 |
| 773             | 0.0101 | 0.0322 |
| 823             | 0.0188 | 0.0554 |
Table S6.
Root-mean square deviation to compare calculation conversion and experimental conversion for the reduction of $\text{In}_2\text{O}_3$.

| Temperature / K | Root Mean Square Deviation |
|----------------|---------------------------|
|                | R3           | AE1          |
| 723            | 0.0068       | 0.0076       |
| 773            | 0.0029       | 0.0157       |
| 823            | 0.0100       | 0.0197       |
| 873            | 0.0070       | 0.0173       |
| Oxide         | Kinetic model | Reaction rate constant $k / 10^3$ min$^{-1}$ |
|--------------|---------------|-----------------------------------------------|
|              |               | $673$ K | $723$ K | $748$ K | $773$ K | $823$ K | $873$ K |
| Cu-In$_2$O$_3$ | R2            | 0.402   | 0.785   | -       | 1.203   | 1.763   | -       |
| 10wt% Cu/In$_2$O$_3$ | R3            | -       | 0.529   | 0.820   | 1.166   | 1.574   | -       |
| In$_2$O$_3$ | R3            | -       | 0.008   | -       | 0.028   | 0.047   | 0.074   |
Table S8.
Root-mean square deviation to compare the calculation conversion and the experimental conversion for the oxidation of Cu-In$_2$O$_3$.

| Temperature / K | Root Mean Square Deviation |  |
|----------------|----------------------------|---|
|                | R2 | R1 | R2 (x < 0.8) | R1 (x < 0.8) |
| 673            | 0.1050 | 0.0435 | 0.1263 | 0.0178 |
| 723            | 0.0773 | 0.1144 | 0.0950 | 0.0058 |
| 748            | 0.0838 | 0.1253 | 0.1041 | 0.0130 |
| 773            | 0.0511 | 0.1560 | 0.0686 | 0.0190 |
| 798            | 0.0427 | 0.1865 | 0.0576 | 0.0149 |
| 823            | 0.0597 | 0.1728 | 0.0779 | 0.0149 |
Table S9.
Root-mean square deviation to compare the calculation conversion and the experimental conversion for the oxidation of 10wt% Cu/In$_2$O$_3$.

| Temperature / K | Root Mean Square Deviation |
|-----------------|----------------------------|
| 723             | 0.0297                     |
| 773             | 0.0178                     |
| 798             | 0.0167                     |
| 823             | 0.0158                     |
Table S10.
Root-mean square deviation to compare the calculation conversion and the experimental conversion for the oxidation of \( \text{In}_2\text{O}_3 \).

| Temperature / K | Root Mean Square Deviation
|-----------------|----------------------------------|
|                | AE1                              |
| 723            | 0.0230                           |
| 748            | 0.0221                           |
| 773            | 0.0252                           |
| 798            | 0.0220                           |
| 823            | 0.0206                           |
| Oxide         | Kinetic model | Reaction rate constant $k / 10^3$ min$^{-1}$ | 673 K | 723 K | 748 K | 773 K | 798 K | 823 K |
|--------------|--------------|---------------------------------------------|-------|-------|-------|-------|-------|-------|
| Cu-In$_2$O$_3$ | R1           | 0.284                                       | 0.614 | 0.789 | 0.956 | 1.307 | 1.456 |
| 10wt% Cu/In$_2$O$_3$ | AE1         | -                                           | 0.785 | -     | 1.944 | 2.443 | 3.505 |
| In$_2$O$_3$   | AE1          | -                                           | 0.894 | 1.526 | 2.549 | 3.438 | 5.147 |
Reference

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Fast oxygen ion migration in Cu–In–oxide bulk and its utilization for effective CO$_2$ conversion at lower temperature

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Electronic Supplementary Information (ESI) available: [experimental procedure, supporting data etc.]. See DOI: 10.1039/x0xx00000x
Efficient activation of CO₂ at low temperature was achieved by reverse water–gas shift (RWGS-CL) by virtue of fast oxygen ion migration in Cu-In–structured oxide, even at lower temperatures. Results show that novel Cu-In₂O₃ structured oxide can show a remarkably higher CO₂ splitting rate than ever reported. Various analyses revealed that RWGS-CL on Cu-In₂O₃ is derived from reducible between Cu–In₂O₃ and CuIn alloy. Key factors for high CO₂ splitting were fast migration of oxygen ions in alloy and the preferential oxidation of the interface of alloy–In₂O₃ in the bulk of the particles. The findings reported herein can open up new avenues to achieve effective CO₂ conversion at lower temperatures.

Anthropogenic emissions of greenhouse gases (GHGs) are regarded as a cause of global warming, which is expected to lead to severe future climate change. Particularly, carbon dioxide (CO₂) derived from fossil fuels and industrial processes has long presented strong effects that continue to raise global mean temperatures 1,2. Therefore, development of CO₂ capture and utilization (CCU) technologies 3–6 represents an urgent task for reducing CO₂ emissions into the atmosphere and for establishing a sustainable carbon cycle. Synthesis of fuels using electricity generation from renewable resources and using CO₂, most notably sun-to-fuel (STF) 3 and power-to-liquids 4 processes, has been proposed as a means of developing CCU. In fact, CO₂-based fuels are anticipated as a technology that can increasingly incorporate renewable energy into the mobility sector as an “e-fuel” 5,6. For these fuel production technologies, the potential process route is a Fischer–Tropsch (FT) process using syngas, which includes hydrogen and carbon monoxide (CO) converted from captured CO₂ 3–4.

As a method of efficient conversion of CO₂ to CO through this process, reverse water–gas shift (RWGS) is a promising reaction that uses renewable H₂ 10,11. Mallapragada et al. proposed that the STF route consisting of RWGS followed by the FT reaction has higher efficiency than that of other routes with direct CO₂ conversion by photosynthetic bacteria and biomass conversion 5. The RWGS is an equilibrium limited reaction (equation 1) with an endothermic nature.

\[
\text{CO}_2 + H_2 \leftrightarrow \text{CO} + H_2O \quad \Delta H_{298}^0 = 42.1 \text{ kJ mol}^{-1}
\]

This reaction requires high reaction temperatures, separation of gas products to gain high conversion, and a suitable H₂/CO ratio syngas. Furthermore, conventional catalytic RWGS processes involve side reactions, as presented in the following equations 2 and 3.

\[
\text{CO}_2 + 3H_2 \leftrightarrow \text{CH}_4 + 2H_2O \quad \Delta H_{298}^0 = -206.5 \text{ kJ mol}^{-1}
\]

\[
\text{CO}_2 + 4H_2 \leftrightarrow \text{CH}_4 + 2H_2O \quad \Delta H_{298}^0 = -165 \text{ kJ mol}^{-1}
\]

The CH₄ produced via these side reactions makes gas separation more complex. Additionally, it loses energy because of the exothermic reaction. One solution for this shortcoming is using chemical-looping reverse water–gas shift (RWGS-CL) 12,13. The overall concept of solar-driven fuel (chemical) synthesis process with RWGS-CL is presented in Fig. 1. Through this process, CO₂ is converted to CO in two separate steps: reduction and re-oxidation of a metal oxide as an oxygen storage material (OSM). First, OSM is reduced by H₂ (reaction 4). Subsequently, the reduced OSM is re-oxidized by CO₂ to generate pure CO (reaction 5).

\[
\text{MO}_x + \delta H_2 \rightarrow \text{MO}_x-\delta + \delta H_2O \quad (4)
\]

\[
\text{MO}_{x-\delta} + \delta CO_2 \rightarrow \text{MO}_x + \delta CO \quad (5)
\]

Actually, RWGS-CL has benefits deriving from the absence of undesirable side reactions, which drives the equilibrium to CO production, and simplified gas separation, which leads to its improved energy efficiency. In fact, Wenzel et al. investigated solar-to-syngas efficiency for RWGS-CL processes and reported that the energy demand for separation is reduced by 77% compared to conventional RWGS processes 14. In the RWGS-CL process, the development of OSM is an indispensable factor to make this process feasible. The rates of reduction and oxidation, CO yield, and stability are emphasized as key factors affecting OSM for the RWGS-CL cycles. Furthermore, the operation temperature is an important factor. Isothermal operation at lower temperatures is desired to reduce heat loss and to increase its feasibility 15. In recent years, great effort has been put forth for the development of OSMs with high redox property for RWGS-CL 13–16. This study has revealed that indium-based oxide can be a novel OSM material able to exhibit extremely high isothermal RWGS-CL performance at low temperatures (673–773 K). Particularly, the performance of Cu-modified In₂O₃ formed from CuInO₃ as a parent material was found to be promising for this purpose. Characterizations of OSMs were conducted using powder X-ray diffraction (XRD), a field emission transmission electron microscope equipped with an energy-dispersive X-ray spectrometer (STEM-EDX), X-ray photoelectron spectroscopy (XPS), and in-situ X-ray absorption fine structure (XAFS) measurements.
Isothermal RWGS-CL performance

After applying various oxides for RWGS-CL, we found that Cu–In–mixed oxide has high potential for this RWGS-CL. The CO$_2$ splitting performance obtained in this study is presented in Fig. 2 and Table S1 along with results described in earlier reports of the literature. Compared to other perovskite-type oxides, which were reported earlier, Cu–In$_2$O$_3$ showed higher CO$_2$ splitting amounts and rates even at low temperatures such as 673–773 K. Among all the oxides, Cu–In$_2$O$_3$ derived from Cu$_2$In$_2$O$_5$ is the most promising material for low-temperature isothermal RWGS-CL. The cycle performance of isothermal RWGS-CL on Cu$_2$In$_2$O$_5$ at 773 K is presented in ESI Fig. S1. The reduction and oxidation (redox) amounts are defined as the moles of oxygen released or restored per gram of Cu$_2$In$_2$O$_5$. At the first cycle, Cu$_2$In$_2$O$_5$ showed reduction of 9.50 mmol g$^{-1}$ and re-oxidation of 4.82 mmol g$^{-1}$. Then, at cycles 2–5, the reduction and the oxidation amounts were, respectively, 5.06 ± 0.41 mmol g$^{-1}$ and 4.80 ± 0.40 mmol g$^{-1}$. Excess reduction at the first cycle (= 4.68 mmol g$^{-1}$) was almost equivalent to the release of 2 mol oxygen atoms per mol of Cu$_2$In$_2$O$_5$. This finding suggests that Cu$_2$In$_2$O$_5$ has become Cu(0)–In$_2$O$_3$, which is confirmed later. Products of RWGS-CL were measured using a quadrupole mass spectrometer. The mass spectra of products are presented in ESI Fig. S2. The products at reduction and oxidation steps were identified respectively as H$_2$O (m/z = 18) and CO (m/z = 28) without production of other by-products. Results confirmed that RWGS-CL on Cu–In$_2$O$_3$ formed from Cu$_2$In$_2$O$_5$ is a selective CO$_2$ conversion to CO.

Structural characterization for this material was achieved using powder XRD, STEM-EDX, and in-situ XAFS measurements. The XRD patterns obtained from fresh and post-reaction samples are portrayed in Fig. 3A. The XRD pattern of the fresh sample showed the formation of Cu$_2$In$_2$O$_5$ with no impurity phase. The XRD pattern of the reduced sample exhibited diffraction peaks assigned to Cu$_x$In$_y$ alloy and In$_2$O$_3$. The main compositions of the alloy were Cu$_7$In$_3$ and Cu$_9$In$_4$. Then, after the oxidation step, diffraction peaks of Cu$_x$In$_y$ alloy disappeared. Those of Cu metal and In$_2$O$_3$ were observed. STEM-EDX images are presented in Figs. 3C, D and ESI Fig. S3. The SEM micrographs taken of the reduced Cu–In$_2$O$_3$ (ESI Fig. S3A) show the presence of ca. 1 µm particles. The elemental composition of the particles was identified using EDX mapping (copper, red; indium, green; oxygen, blue). Results of EDX mapping of the sample after reduction (Fig. 3C and
ESI Fig. S3A show that indium is distributed evenly over the particle, whereas copper is localized; oxygen is scattered. These images indicate Cu–In alloy formation by reduction. For the re-oxidized sample, many particles with uniformly distributed copper, indium, and oxygen were observed as depicted in Fig. 3D and ESI Fig. S3B. Using image processing and analysis for these EDX images with Python (see ESI text for details), it was estimated that 84% of In exists as overlapping with Cu, and that 93% of Cu exists as overlapping with In. These results demonstrate that the fine matrix of Cu–In–O was formed in the re-oxidized particle. The Cu in re-oxidized particles was regarded as highly distributed on the surface, or incorporated into the In$_2$O$_3$ structure. As additional information, in-situ XAFS results are presented in Figs. 3E and 3F (see ESI text and Figs. S5–S7 for details). The sequential change of In K-edge XANES spectra indicates that the redox of In(III) $\approx$ In(0) occurs during the RWGS-CL cycle. By contrast, Cu K-edge XANES spectrum, which only slightly changed during the RWGS-CL cycle, represented the formation of Cu–In alloy $^{17,18}$. This structural information obtained from XRD, STEM-EDX, and XAFS measurements demonstrates that the RWGS-CL cycle on Cu–In$_x$O$_y$, as a parent material, is based on the redox of indium with the formation and oxidation of Cu–In alloy. This material during RWGS-CL is designated hereinafter as Cu–In$_x$O$_y$.

To elucidate the role of Cu in Cu–In$_x$O$_y$, we compared the performance of isothermal RWGS-CL as a function of temperature on Cu–In$_3$O$_5$ (derived from Cu$_3$In$_5$O$_{15}$), 10wt% Cu/In$_2$O$_3$ (A), and In$_2$O$_3$ (C). Reduction was conducted in 10% H$_2$ atmosphere for 30 min; oxidation was conducted in 10% CO$_2$ atmosphere.

Fig. 4 Dependence of RWGS-CL performance of each oxide on the reaction temperature. Amounts of redox and average CO$_2$ splitting during re-oxidation step on Cu–In$_3$O$_5$ (A), 10wt% Cu/In$_2$O$_3$ (B), and In$_2$O$_3$ (C). Reduction was conducted in 10% H$_2$ atmosphere for 30 min; oxidation was conducted in 10% CO$_2$ atmosphere.

Reduction step by H$_2$. Temperature-programmed reduction by H$_2$ (H$_2$-TPR) measurements, the results of which are presented in Fig. 5A, was done to investigate the reducibility of oxides. The ESI presents additional details.

![Fig. 5. Kinetic analysis for each oxide at the reduction step.](image)

**Fig. 5.** Kinetic analysis for each oxide at the reduction step. (A) H$_2$-TPR profiles for Cu–In$_x$O$_y$ (derived from Cu$_3$In$_5$O$_{15}$), 10wt% Cu/In$_2$O$_3$, and In$_2$O$_3$. (B) Arrhenius plots for the reduction of Cu–In$_x$O$_y$ (derived from Cu$_3$In$_5$O$_{15}$), 10wt% Cu/In$_2$O$_3$, and In$_2$O$_3$.

For Cu-containing oxides (Cu–In$_x$O$_y$ and 10 wt% Cu/In$_2$O$_3$), the H$_2$-TPR profiles showed three notable reduction areas (ca. 400–550 K, 580–700 K, and 700–920 K). In the moderate temperature region of 580–700 K, the amount of reduction was equivalent to about 26% of oxygen contained in Cu$_3$In$_5$O$_{15}$. Therefore, the reduction of In(III) with the formation of Cu–In$_x$ alloy, the composition of which finally approached CuIn$_3$, was regarded as proceeding in this moderate temperature region. Regarding results of H$_2$-TPR measurements, results show that Cu species promote the reduction of indium oxide at low temperatures. To investigate more details of the mechanism, the kinetic model for the reduction of these oxides was verified using the method presented by Hancock and Sharp for the isothermal solid-state reaction $^{19-21}$. The ESI text, Figs. S12–S15 and Tables S4–S6 present additional details. Kinetic models used for model fitting are shown in ESI Table S3. As a result of the investigations, the phase-boundary-controlled reaction models (R2 and R3 model) were found to be suitable to describe experimentally obtained data for all the oxides. These models are categorized to a classic shrinking core model in which the rate-controlling step is the surface chemical reaction $^{20,21}$. The activation energy was investigated using the reaction rate constant $k$ values obtained from the model fitting described above (ESI Table S7). Plots of ln($k$) vs. 1/T (Arrhenius plot) for the three oxides are presented in Fig. 5B. The respective activation energies for Cu–In$_2$O$_3$ (45.2 kJ mol$^{-1}$) and 10 wt% Cu/In$_2$O$_3$ (53.4 kJ mol$^{-1}$) were much lower than that for In$_2$O$_3$ (76.6 kJ mol$^{-1}$), confirming that the Cu species supported on In$_2$O$_3$ decreased the activation barrier for reactions between the surfaces of In$_2$O$_3$ and H$_2$. The slight difference in the activation energy between Cu–In$_2$O$_3$ and 10 wt% Cu/In$_2$O$_3$ suggests that the effect of the Cu species on the reduction does not depend much on these morphologies.

Oxidation step by CO$_2$ for CO formation. Next, kinetic investigations were conducted of the oxidation step by CO$_2$ in the RWGS-CL cycle. The kinetic model for the oxidation
of the oxide was also verified using the Hancock and Sharp method. As a consequence of the model fitting (details of which are presented in ESI Figs. S16–S19 and Tables S8–S10), the most suitable models were concluded to be a Zero-order model (R1 model) \(^{19-21}\) for \(\text{Cu-In}_2\text{O}_3\) and the nucleation model, known as the Avrami–Erofe’ev model (AE1 model), for the other two oxides \(^{22-24}\). Figure 6A presents the Arrhenius plot for the oxidation of these three oxides. The reaction rate constant \(k\) values obtained from model fitting are presented in Table S11. The activation energy for \(\text{Cu-In}_2\text{O}_3\) is 50.7 kJ mol\(^{-1}\), which is markedly lower than that for either of the other two oxides. As results of the model fitting show, the large difference in the activation energy is attributable to the different mechanisms of oxidation among these oxides. Considering that AE1 is suitable as a model for \(\text{In}_2\text{O}_3\) and 10 wt% Cu/\(\text{In}_2\text{O}_3\), results show that the overall oxidation of these two oxides is determined by the rate of formation and growth of the indium oxide nuclei. At the beginning of the reaction, the rate of oxidation is high because of random nucleation on the surface of the reduced oxide. However, as the nucleation and nuclei growth proceed, the rate of oxidation plummets because of the decrease of the reduced surface. As a result, a long time is necessary to complete oxidation by CO\(_2\).

![Fig. 6. Kinetic analysis of each oxide at re-oxidation steps. (A) Arrhenius plots for the oxidation of \(\text{Cu-In}_2\text{O}_3\) (derived from \(\text{Cu}_2\text{In}_3\text{O}_8\)), 10wt% Cu/\(\text{In}_2\text{O}_3\) and \(\text{In}_2\text{O}_3\). (B) Dependence of differential CO\(_2\) splitting rate on conversion of oxides. (C) Surface In/O ratios on \(\text{Cu-In}_2\text{O}_3\) and 10wt% Cu/\(\text{In}_2\text{O}_3\) during re-oxidation step. (D) Presumed mechanism for CO\(_2\) splitting on the reduced \(\text{Cu-In}_2\text{O}_3\).](image)

Figure 6B presents different rates of CO\(_2\) splitting over these oxides during oxidation by CO\(_2\). For all oxides, the degree of reduction before re-oxidation was fixed at 3.0 mmol g\(^{-1}\). On \(\text{In}_2\text{O}_3\) and 10 wt% Cu/\(\text{In}_2\text{O}_3\), the CO\(_2\) splitting rate decreased drastically with the progress of oxidation. The oxidation of \(\text{Cu-In}_2\text{O}_3\) proceeded while maintaining a constant CO\(_2\) splitting rate of about 340 \(\text{µmol g}^{-1}\text{min}^{-1}\) until conversion reached 60%. As a result, re-oxidation of the reduced \(\text{Cu-In}_2\text{O}_3\) is completed twice as rapidly as those of the other two oxides. These results obtained from the kinetic investigation for \(\text{Cu-In}_2\text{O}_3\) suggest that the amount of the active site for CO\(_2\) splitting remains constant while oxidation is proceeding. Figure 6C shows the surface In/O ratio at each oxidation rate of the reduced \(\text{Cu-In}_2\text{O}_3\) and 10wt% Cu/\(\text{In}_2\text{O}_3\), as measured by XPS. The In/O ratio of the \(\text{Cu-In}_2\text{O}_3\) surface remained above 0.9, even at the oxidation rate of 75%, which indicates that bulk oxidation proceeds preferentially while the surface remains in a highly reduced state. This particular CO\(_2\) splitting mechanism of \(\text{Cu-In}_2\text{O}_3\) is explainable as shown in Figure 6D. First, CO\(_2\) splits on the surface of \(\text{Cu-In}\) alloy; the CO and oxide ion (O\(^{2-}\)) are generated. Subsequently, the O\(^{2-}\) migrates to the bulk of the particle. It presumably oxidizes the \(\text{Cu-In}\) alloy–\(\text{In}_2\text{O}_3\) interface. As a result, the alloy surface, as the active site, remains in a highly reduced state. Rapid CO\(_2\) splitting proceeds continuously.

**Conclusion**

As reported herein, \(\text{Cu-In}_2\text{O}_3\) was synthesized. Then its performance for RWGS-CL was investigated at the low temperatures of 673–773 K. Results of RWGS-CL cycle tests demonstrated that, even at low temperatures, \(\text{Cu-In}_2\text{O}_3\) exhibited much higher CO\(_2\) splitting performance than ever reported. Results of XRD, STEM-EDX, and in-situ XAFS measurements showed that the oxide has a structure of reduced Cu supported on \(\text{In}_2\text{O}_3\) (\(\text{Cu-In}_2\text{O}_3\)) under the RWGS-CL condition, and showed that its redox property is based on Cu/\(\text{In}_2\text{O}_3\) alloy formation and re-oxidation. In addition, because low performance was exhibited by pure \(\text{In}_2\text{O}_3\) and Cu supported \(\text{In}_2\text{O}_3\) that were prepared using an impregnation method, the structured state of \(\text{Cu-In}_2\text{O}_3\) has extremely important roles for its high RWGS-CL performance. \(\text{H}_2\)-TPR and kinetic investigations revealed that \(\text{Cu-In}_2\text{O}_3\) shows high reducibility, even at low temperatures. We concluded that Cu species promote the reaction of \(\text{H}_2\) with the oxide surface. Results of kinetic investigations in the oxidation step indicate that the Cu/\(\text{In}_2\text{O}_3\) particle surface conserved a highly reduced state, even in a re-oxidation condition, resulting in rapid completion of re-oxidation by CO\(_2\). The interesting oxidation behavior is attributed to rapid O\(^{2-}\) migration from the surface to bulk of the \(\text{Cu-In}\) alloy and preferential oxidation of the interface of alloy–\(\text{In}_2\text{O}_3\). The combination of high reducibility and the specific re-oxidation mechanism engenders the high performance found for RWGS-CL on \(\text{Cu-In}_2\text{O}_3\).

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**Conflicts of interest**

There are no conflicts to declare.
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