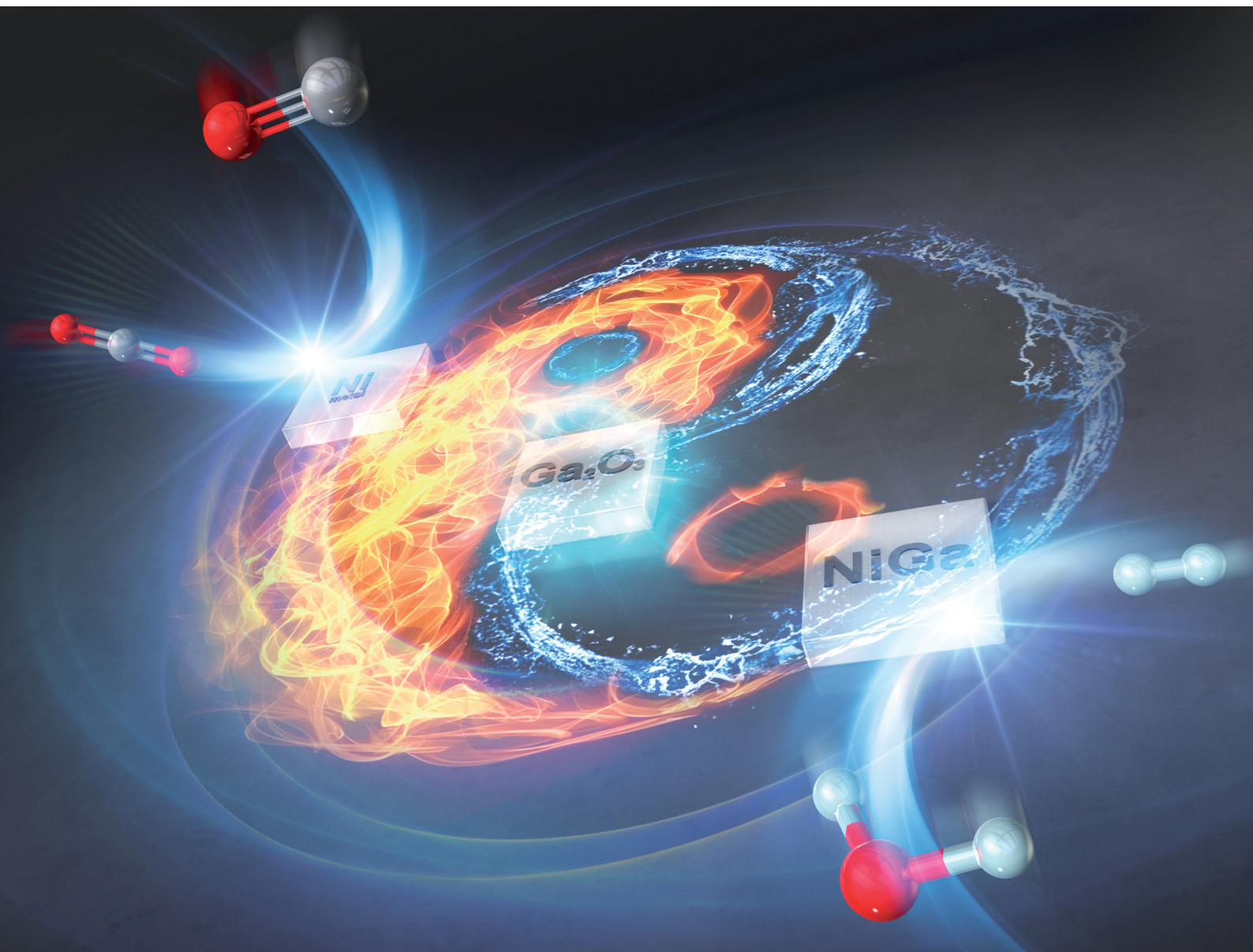


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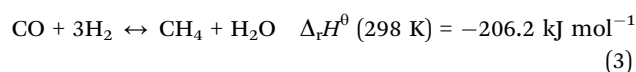
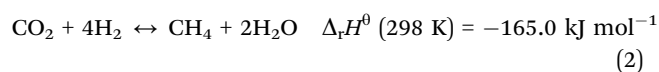
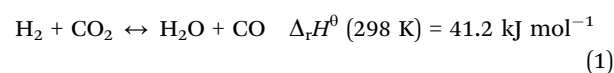
Equilibrium unconstrained low-temperature CO₂ conversion on doped gallium oxides by chemical looping†

Keke Kang, Sota Kakihara, Takuma Higo,  Hiroshi Sampei,  Koki Saegusa and Yasushi Sekine  *

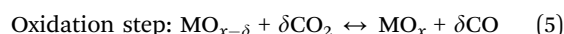
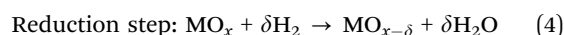
Reverse water gas shift (RWGS) can convert CO₂ into CO by using renewable hydrogen. However, this important reaction is endothermic and equilibrium constrained, and thus traditionally performed at 900 K or higher temperatures using solid catalysts. In this work, we found that RWGS can be carried out at low temperatures without equilibrium constraints using a redox method called chemical looping (CL), which uses the reduction and oxidation of solid oxide surfaces. When using our developed MGa₂O_x (M = Ni, Cu, Co) materials, the reaction can proceed with almost 100% CO₂ conversion even at temperatures as low as 673 K. This allows RWGS to proceed without equilibrium constraints at low temperatures and greatly decreases the cost for the separation of unreacted CO₂ and produced CO. Our novel gallium-based material is the first material that can achieve high conversion rates at low temperatures in reverse water gas shift using chemical looping (RWGS-CL). Ni outperformed Cu and Co as a dopant, and the redox mechanism of NiGa₂O_x is a phase change due to the redox of Ga during the RWGS-CL process. This major finding is a big step forward for the effective utilization of CO₂ in the future.

As a greenhouse gas, carbon dioxide (CO₂) is emitted excessively from fossil fuel combustion, causing severe environmental difficulties.^{1,2} Therefore, to achieve carbon neutrality, developing CO₂ capture and utilization (CCU) technologies that can accommodate sustainable recycling^{3–6} is pivotally important. The reverse water gas shift (RWGS) reaction (eqn (1)) is a promising catalytic method to achieve “CO₂-to-CO” conversion using renewable H₂ as a reductant. The produced CO can be used flexibly for both methanol (MeOH) synthesis and downstream Fischer-Tropsch (F-T) processes to produce various liquid chemicals and fuels.^{7,8} However, conventional RWGS is an endothermic and reversible reaction associated with

shortcomings such as high operating temperature, equilibrium constraints, unwanted side reactions of methanation (eqn (2) and (3)) and complicated separation of gaseous products.³



Conducting RWGS *via* chemical looping (RWGS-CL) can resolve the shortcomings of conventional processes because it can be separated into two sub-reactions (eqn (4) and (5)) using oxygen storage materials (OSMs). Consequently, the reduction (eqn (4)) and oxidation (eqn (5)) reactions can proceed at separate steps and sites.



In this way, the OSMs can be prevented from making contact with the products, thereby eliminating side reactions and simplifying gas separation. Reportedly, by evaluation of the solar-to-syngas energy efficiency, RWGS-CL can save 77% of the energy used for gas separation compared to conventional RWGS.⁹ Moreover, RWGS-CL makes it possible to break the equilibrium barrier by the application of appropriate OSMs, thereby further improving energy efficiency and conserving energy. More importantly, the overall route for producing chemicals and fuels with RWGS-CL (Fig. S1, ESI†) can be carbon-neutral and sustainable if solar, electrical, or other non-fossil energy is used for hydrogen generation (*e.g.*, water splitting).¹⁰

The redox performance of OSMs is crucially important for RWGS-CL. Recently, much progress has been made to develop OSMs with excellent RWGS-CL performance, such as perovskite-structured oxides,^{8,11–18} spinel-structured oxides,^{19–21} Fe-based

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oxides,^{19–22} and In-based oxides.^{23,24} Although experimental conditions such as H₂ or CO₂ feed gas concentrations and detection methods are not all the same in those studies, a recent report described that Co–In oxide showed the best CO₂ splitting rate of 0.28 mmol min^{−1} g^{−1} and a redox amount of 3.25 mmol g^{−1} at 773 K in comparison to other reported materials.²⁴ However, in practice, the low CO₂ equilibrium conversion of the oxidation step leads to a low concentration of the produced CO (the ratio of (CO/CO + CO₂)), increasing the cost of separating CO from CO₂ in the overall route with RWGS-CL (highlighted red box in Fig. S1, ESI†). Therefore, it is necessary to find proper OSMs that can make the oxidation step proceed forward rapidly even with a high CO concentration. Nevertheless, no study reported to date has particularly addressed this matter. Reportedly, the CO₂ oxidation step can proceed forward on Co–In₂O₃ with a 70–80% concentration of CO in the medium temperature region, but CO was not introduced simultaneously when evaluating the RWGS-CL performance.²⁴

In this work, novel MGa₂O₄ (M = Ni, Cu, Co) spinel structured oxides were developed as OSMs with almost 100% CO₂ conversion even at lower temperature and Ni outperforms Cu and Co as a dopant in the redox amount and CO₂ splitting rate. The method for measuring the maximum CO₂ conversion of the oxidation step, the procedure for the RWGS-CL cycling test and the related definitions for evaluating the performance are also described in the ESI† text.

To elucidate the reaction mechanisms of the NiGa₂O₄ material, powder X-ray diffraction (XRD), transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDX), Brunauer–Emmett–Teller (BET) measurement and *in situ* X-ray absorption fine structure (*in situ* XAFS) were conducted to characterize the structural features. Moreover, the redox behaviors of the MGa₂O₄ (M = Ni, Cu, Co) oxides were characterized by H₂ temperature-programmed reduction (H₂-TPR) and CO₂ temperature-programmed oxidation (CO₂-TPO). Kinetics analysis was also conducted to elucidate the oxidation behavior of NiGa₂O₄ with 90% CO–10% CO₂ when using the Ozawa–Flynn–Wall (OFW) method (details in the ESI†).

Comparison between the maximum CO₂ conversion of MGa₂O₄ (M = Ni, Cu, Co) and earlier reported In-based materials for RWGS-CL and the equilibrium conversion of conventional RWGS is presented in Fig. 1A, and the experimentally obtained data for MGa₂O₄ are presented, respectively, in the ESI† text and in Fig. S2–S5 (ESI†). Ga metal is known to have a very low melting point (302.8 K) on its own when reduced, but in this study Ga always remained in a composite (alloyed) state with other metals, and no melting or volatilization was observed before or after H₂ reduction. Actually, Cu–In₂O₃ and Co–In₂O₃ were both reported to show superior fast kinetics at medium temperatures. However, Cu–In₂O₃ showed no advantage for CO₂ conversion compared with the conventional RWGS.²⁵ Although Co–In₂O₃ displayed a maximum CO₂ conversion of 70–80% in the medium temperature region, which is higher than that of conventional RWGS, there is some room for improving it to conserve energy and decrease costs. Regarding MGa₂O₄ (M = Ni, Cu, Co), they showed a maximum CO₂ conversion of 99% at temperatures in the range of 673–973 K,

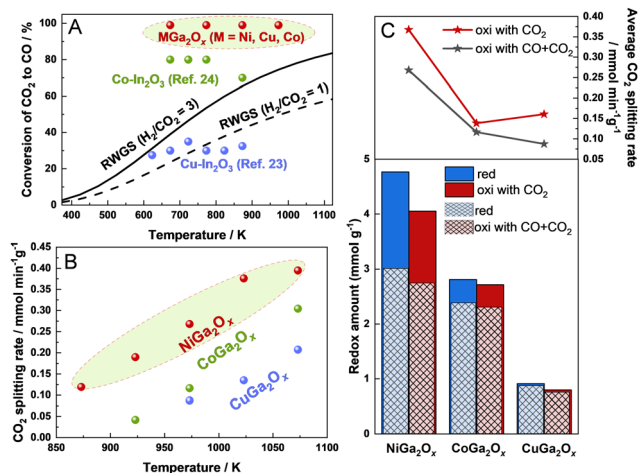


Fig. 1 (A) The maximum CO₂ conversion of Ga-based and In-based oxides for RWGS-CL and the equilibrium conversion of conventional RWGS. (B) The CO₂ splitting rates of MGa₂O₄ (M = Ni, Cu, Co) under a 90% concentration of CO. The data of CoGa₂O₄ were collected before reaching a stable state. (C) The redox amounts and average splitting rates of MGa₂O₄ (M = Ni, Cu, Co) at 973 K.

which is much higher than the equilibrium conversion of conventional RWGS and the materials reported earlier. This result indicates MGa₂O₄ (M = Ni, Cu, Co) as promising RWGS-CL materials with superior thermodynamical advantages.

The redox amounts and CO₂ splitting rates of NiGa₂O₄ and CuGa₂O₄ were all measured after sufficient H₂ pretreatment at 973 K until the following cycles became stable, but it is difficult for CoGa₂O₄ to reach a stable state, even when pretreated at a higher temperature for its low reduction rate, as confirmed by the combination of redox amounts and XRD (related descriptions are presented in Fig. S6 and S7, ESI†). Deeper pre-reduction at high temperatures will aggregate the particles and shrink the surface area (the results of BET are presented in Table S1, ESI†), consequently deteriorating the RWGS-CL performance. Therefore, we infer CoGa₂O₄ as an unsuitable material for RWGS-CL. However, the performance data of CoGa₂O₄ without reaching a stable state will still be presented as a comparison for the following discussion. The CO₂ splitting rates of MGa₂O₄ (M = Ni, Cu, Co) with 90% CO–10% CO₂ at different temperatures are shown in Fig. 1B. NiGa₂O₄ shows high average CO₂ splitting rates of 0.12, 0.19, 0.27, 0.38, and 0.39 mmol min^{−1} g^{−1} at 873, 923, 973, 1023, and 1073 K, respectively, even under a 90% concentration of CO, which is markedly higher than those of CoGa₂O₄ and CuGa₂O₄.

The CO₂ splitting rates and redox amounts of MGa₂O₄ (M = Ni, Cu, Co) at 973 K under different oxidation conditions (10% CO₂; 90% CO–10% CO₂) are presented in Fig. 1C. Generally, oxidation with CO + CO₂ decreases both the redox amounts and the CO₂ splitting rate compared with oxidation with only CO₂ because of the backward progress of the reverse reaction. Ni is a better dopant than Co and Cu in terms of the redox amount and CO₂ splitting rate under both CO₂ and CO + CO₂ oxidation conditions. The experimental results (Fig. S8 and ESI† text) indicate no by-product formation and negligible carbon



deposition using a fixed bed reactor equipped with a quadrupole mass spectrometer (Q-MS), which show the reliability and repeatability of our method. Moreover, comparisons of the CO₂ splitting rates and CO yields of the OSMs for RWGS-CL in the present work (with 10% CO₂) and in the literature are presented in Fig. S9 (ESI[†]). Actually, NiGa₂O_x shows a relatively high CO₂ splitting rate and CO yield compared to those of the other reported OSMs.^{8,11,13,16,19–21,26–28} In summary, NiGa₂O_x showed high potential for RWGS-CL and was therefore selected for further study. The stability results of NiGa₂O_x over 10 cycles at 973 K are shown in Fig. S10 (ESI[†]), exhibiting a slow decrease in the oxidation amounts and CO₂ splitting rates during cycling, which is partially attributable to the deep pre-reduction and repetitive cycles leading to partial shrinkage of the surface area of the material. The STEM-EDS results in Fig. S11 and BET results in Table S1 confirm the structure stability even after 10 cycles of reaction (details in the ESI[†]).

H₂-TPR measurements were conducted on different metal oxide samples for RWGS-CL analysis (Fig. 2A). Ga₂O₃ shows almost no reduction in the tested temperature range, the dopants of Ni, Co and Cu improve the reducibility of Ga₂O₃ to a different extent. NiGa₂O_x exhibited a significantly higher H₂ consumption amount which started at a much lower temperature compared to CoGa₂O_x or CuGa₂O_x, indicating the dopant of Ni outperforms Cu or Co in reducibility. Similarly, CO₂-TPO measurements (Fig. 2B) confirmed that the Ni dopant also outperforms Cu or Co in the oxidation ability. NiGa₂O_x also shows a much higher surface area both after reduction and after oxidation than CoGa₂O_x or CuGa₂O_x according to the BET results (Table S1, ESI[†]). A larger surface area provides more reaction sites, allowing more reactant molecules to participate in the reaction simultaneously, leading to a better reaction rate for NiGa₂O_x. Moreover, the results of density functional theory (DFT) calculations show that the Ni-doping material displays a better CO adsorption ability than the other two, which is beneficial for Ni outperforming Cu and Co as a dopant (details in Fig. S12–S14 and Table S2 and ESI[†] text).

Structural and electronic properties were investigated using XRD, STEM-EDX, BET, and *in situ* XAFS. From the XRD spectra in Fig. 3A (left), the as-prepared sample shows only peaks of the NiGa₂O₄ spinel, manifesting the successful preparation of the target material. From the STEM-EDX images of the as-prepared NiGa₂O₄ (Fig. 3A (right)), details in Fig. S15, ESI[†]), tens of

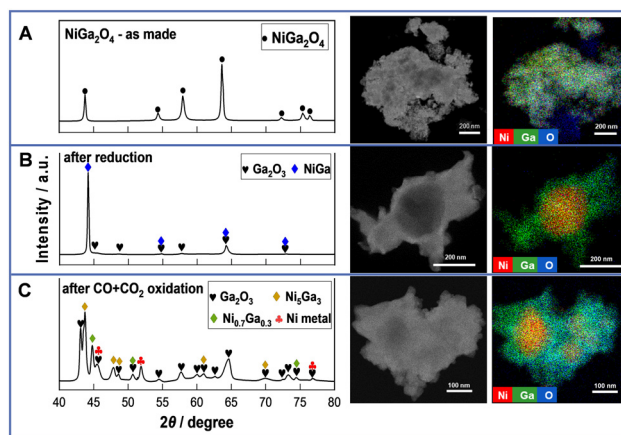


Fig. 3 XRD profiles (left) and STEM-EDX images (right) of NiGa₂O_x (A) as-prepared, (B) after reduction and (C) after CO + CO₂ oxidation.

nanometers of polycrystalline particles are observed. The Ni and Ga species are all dispersed uniformly. Regarding the reduced NiGa₂O_x, the XRD profile exhibits peaks for the NiGa alloy and Ga₂O₃. Also, STEM-EDX images (Fig. 3B (right)) show aggregated Ni species during uniform dispersion of the Ga species. Moreover, the surface area is markedly reduced after the reduction because of the alloy formation. These findings manifest that all NiO and part of Ga₂O₃ are reduced to form the NiGa alloy, thus leaving part of the Ga₂O₃ unreduced. For the CO + CO₂ oxidized NiGa₂O_x, polycrystalline particles with a size of tens of nanometers are observed from STEM images, indicating that the particles will aggregate to larger ones after reduction and reoxidation by CO + CO₂ processing, thereby leading to a decreased surface area as shown in Table S1 (ESI[†]). Moreover, the XRD patterns display the peaks of Ga₂O₃, Ni metal and Ni–Ga alloy (Ni₅Ga₃ and Ni_{0.7}Ga_{0.3}). STEM-EDX images (Fig. 3C (right)) show consistent results of the partial aggregation of Ni species to form the Ni–Ga alloy during uniform dispersion of Ga species and the remaining part of Ni species. These illustrate that only part of the Ga species in the NiGa alloy are re-oxidized to Ga₂O₃ by CO + CO₂, whereas Ni species remain in a metallic state, acting as a part of the alloy or an individual element throughout the RWGS-CL process. Additionally, from the XRD results of the CO₂-only oxidized NiGa₂O_x shown in Fig. S16 (ESI[†]), only Ni metal and Ga₂O₃ peaks were observed, with no peaks of the Ni–Ga alloy compared with the XRD results of CO + CO₂ oxidized NiGa₂O_x. This finding illustrates that the presence of CO influences the amount of the Ni–Ga alloy which can be re-oxidized in the oxidation step.

The *in situ* XAFS results of NiGa₂O_x at 973 K are presented in Fig. 4. The XANES spectra on the Ga *K*-edge shift negatively to the spectrum of the pre-prepared half-reduced NiGa₂O₄ sample during the reduction and shift positively to the Ga₂O₃ spectrum during the CO + CO₂ reoxidation (Fig. 4A and B). These regular changes on the Ga *K*-edge during the RWGS-CL process provide evidence of the successful redox cycle of gallium. From the spectra of NiGa₂O_x during CO₂ re-oxidation shown in Fig. S17A (ESI[†]), it is apparent that the spectra shift faster and finally

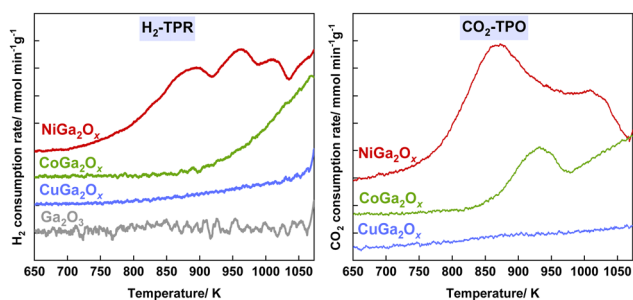


Fig. 2 (A) H₂-TPR and (B) CO₂-TPO of MGa₂O_x (M = Ni, Cu, Co).



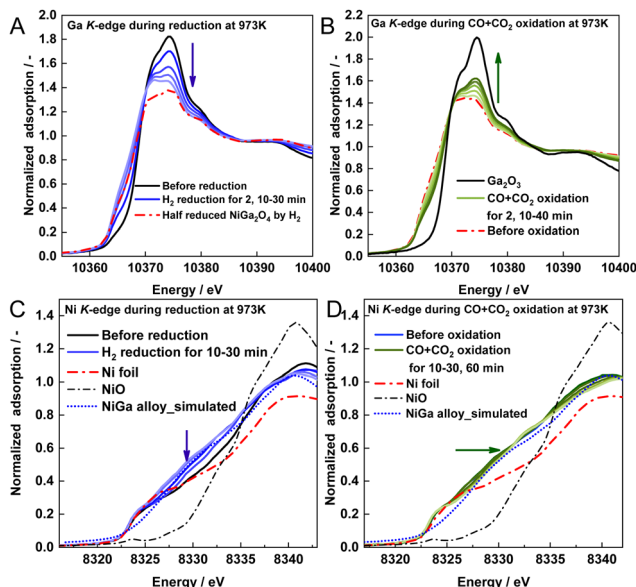


Fig. 4 XANES spectra of NiGa_2O_x during (A) H_2 reduction and (B) $\text{CO} + \text{CO}_2$ oxidation on the Ga K -edge, and (C) H_2 reduction and (D) $\text{CO} + \text{CO}_2$ oxidation on the Ni K -edge.

become closer to that of Ga_2O_3 than that during $\text{CO} + \text{CO}_2$ reoxidation, indicating that the presence of CO in the oxidation step can be expected to restrain the progress of the oxidation of Ga.

From another perspective, Ni K -edge XANES spectra shift negatively toward the direction of the Ni spectrum with a slightly different peak shape during reduction (Fig. 4C) and very similar peak shapes to the simulated NiGa alloy spectrum obtained by calculation (calculation details in the ESI† text), thereby manifesting the formation of the NiGa alloy, except for Ni metal. During $\text{CO} + \text{CO}_2$ reoxidation, the spectra shift slowly to the Ni spectrum (Fig. 4D), manifesting that Ni metals are partially decomposed from the Ni–Ga alloy. Furthermore, the peak shapes are very different from those of NiO, indicating that no NiO was produced during the oxidation. Regarding the spectra of NiGa_2O_x during CO_2 reoxidation in Fig. S17B (ESI†), the spectra shift faster and finally become closer to the Ni spectrum than those during $\text{CO} + \text{CO}_2$ reoxidation. This manifests that the presence of CO in the oxidation step can be expected to restrain the degree of decomposition of the Ni–Ga alloy.

Based on the analyses of structural and electronic properties, the proposed redox mechanism of NiGa_2O_x during the RWGS-CL process in the presence of a high concentration of CO is shown in Fig. S18 (ESI†). Specifically, the Ni–Ga alloy is formed on Ga_2O_3 by H_2 reduction, with formation of oxygen vacancies. Then CO_2 is adsorbed and dissociated on the Ni–Ga alloy with progress of the oxidation step, thereby re-filling the oxygen vacancies. It is worth noting that the presence of CO in the oxidation step influences the NiGa_2O_x performance by restraining the oxygen re-filling, leading to smaller amounts of Ga species for the key phase-change process.

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Conflicts of interest

The authors have no conflicts of interest.

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