

Layered Na₂Ti₃O₇-supported Ru catalyst for ambient CO₂ methanation

Hyo-Jin Kim¹, Kohsuke Mori^{1,2,3*}, Satoshi Ichikawa⁴, Takayoshi Nakano^{1,2}, Hiromi Yamashita^{1,3}

¹Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

E-mail: mori@mat.eng.osaka-u.ac.jp

² Anisotropic Design & Additive Manufacturing Research Center, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan

³ Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, Suita, Osaka 565-0871, Japan.

⁴ Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Ibaraki 567-0047, Japan.

Table of contents

1. Supplementary Methods

2. Ion-exchange of $\text{Na}_2\text{Ti}_3\text{O}_7$ to $\text{Ru}_x\text{Ti}_y\text{O}_z$

- 2.1. Ion-exchange properties with respect to NaHCO_3 concentration
- 2.2. Ion-exchange properties with respect to temperature
- 2.3. Ion-exchange properties with respect to $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ concentration

3. Characterization of Fresh and Used $\text{Ru}_x\text{Ti}_y\text{O}_z$

- 3.1. Characterization of fresh $\text{Ru}_x\text{Ti}_y\text{O}_z$
- 3.2. Importance of layered $\text{Ru}_x\text{Ti}_y\text{O}_z$ structure
- 3.3. Characterization of used $\text{Ru}_x\text{Ti}_y\text{O}_z$ sample

4. Scalability of $\text{Ru}_x\text{Ti}_y\text{O}_z$

5. Supplementary References

Supplementary Methods

Materials and chemicals. Sodium titanate ($\text{Na}_2\text{Ti}_3\text{O}_7$, > 99%) was purchased from Kojundo Chemical Lab. Co., Ltd. P-25 (JRC-TiO-4) was supplied by the Catalysis Society of Japan. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (ReagentPlus®, >99.9%, Ru content 40.00-49.00%), RuO_2 (>99.9%), and Ru black ($\geq 98\%$) were purchased from Sigma Aldrich. Sodium hydrogen carbonate (NaHCO_3 , >99.5%), sodium hydroxide (NaOH , 97%), and nitric acid (HNO_3 , 60%) were purchased from Nacalai Tesque Inc. Activated carbon (FAC-10) was purchased from Osaka Gas Chemicals Co. Ltd.

Preparation of multiple references Ru/TiO_2 (8 wt.%) was prepared by impregnation and calcination to maximize the catalytic activity¹. 8 wt.% condition was selected as an optimum amount between 2, 8, and 16 wt.% condition. Typically, 0.1028 g of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was dissolved in 100 mL of deionized water, following which 0.6 g P-25 was added to the solution with vigorous stirring for 1h. The solution was then evaporated at 70 °C and dried at 100 °C for 3h. The obtained solid was calcined in air at 450 °C for 3 h, at a heating rate of 2 °C min⁻¹. The solid was then washed three times with deionized water to remove residual chlorides. Finally, the sample was dried overnight at 100 °C. With TiO_2 , RuO_2 -No pH adjust, and RuO_2 -pH7 were synthesized under the same condition as $\text{Ru}_x\text{Ti}_y\text{O}_z$ without the addition of $\text{Na}_2\text{Ti}_3\text{O}_7$. In detail, 0.10501 g of NaHCO_3 was dissolved in 25 mL of deionized water and stirred for 30 min at room temperature. Next, 0.11554 g of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was added to the solution with vigorous stirring until no CO_2 bubbles were generated. The pH of the RuO_2 -pH7 sample was adjusted to 7 using NaOH (0.1M NaOH and, in the case of With TiO_2 sample, 0.08 g P-25 was added to the suspension instead of $\text{Na}_2\text{Ti}_3\text{O}_7$. Subsequently, the solution was sealed in stainless-steel autoclave and hydrothermally treated with

vigorous stirring at 160 °C for 24h. Lastly, the solution was cooled to room temperature and filtrated with sufficient water, drying under 100 °C for 6h. RuO₂/Na₂Ti₃O₇ was prepared by physical mixing of RuO₂ and Na₂Ti₃O₇ with same amount of Ru used in Ru_xTi_yO_z synthesis. RuO₂ amount was determined by calculating the molar mass of Ru in RuCl₃·xH₂O was 49 wt.%, which is the possible maximum amount of Ru in RuCl₃·xH₂O precursor. In detail, 0.0745 g of RuO₂ and 0.1 g Na₂Ti₃O₇ were mixed using an agate mortar for 15 min. RuO₂/C, as a state-of-the-art catalyst, was prepared by physical mixing of 75 wt.% RuO₂ with 25 wt.% activated carbon².

FE-SEM/EDS FE-SEM observations and EDS analysis were conducted with JSM-6500F (JEOL, Tokyo, Japan) and Ultima[®] Max (Oxford Instruments, Abingdon-on-Thames, UK) microscopes. All results were collected with an accelerating voltage of 10 kV to minimize sample damage.

STEM-EDS / SAED STEM-EDS and SAED patterns were obtained with a JEOL ARM200F instrument equipped with JED-2300T operating at 200 kV.

High magnification STEM-EDS

STEM-EDS observations were also conducted by Cs-corrected electron microscope ARM-200F (JEOL) at an accelerating voltage of 200kV. EDS maps were acquired using Ru L α line (2.56keV), Ti K α line (4.51keV), and Na K α line (1.04keV), respectively.

XRD XRD spectra were acquired using a Rigaku Ultima IV diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation (λ = 1.5406 Å). Lattice parameters were determined by profile matching with Rietveld and Le Bail refinement using the Profex software.

XPS XPS spectra were collected by ESCA 3400 (Shimadzu, Kyoto, Japan) with a Mg K α radiation source. The binding energies were calibrated by setting the C-C peak at 284.8 eV. Data analysis was performed using CasaXPS. Gaussian (Y%)–Lorentzian (X%) blend (GL(X)) was used for the fitting the carbon species setting to GL(30) line shape as default. Lorentzian asymmetric lineshape (LF (α , β , w , m)) was used for the fitting the ruthenium species (Ru 3d). Specifically, LF (0.8,1.25,500,180) and LF (1.01,1.25,500,50) were applied for the metallic ruthenium doublet (3d_{5/2} and 3d_{3/2}), respectively, and LF (0.25,1,45,280) was used for oxidic ruthenium species, with only minor variation on the α value for the LF term³.

Ex / in - situ XAS / XRD XAS and XRD spectra were collected at BL01B1 beamline station at the SPring-8 facility (JASRI, Harima, Japan) with a Si(111) monochromator. Each sample was prepared in the form of pellet and measured in transmission mode. In the case of *in-situ* XAS/XRD measurement, the sample was placed in a batch-type *in situ* XAS cell. The sample was first exposed under a 20 mL min⁻¹ flow of reaction gas (1 mL min⁻¹ of N₂, 14.25 mL min⁻¹ of H₂, 4.75 mL min⁻¹ of CO₂) and a temperature increase to 140 °C at a rate of 6 °C min⁻¹, and then holding the temperature for 2 h. The temperature was subsequently raised to 300 °C at a rate of 6 °C min⁻¹ and held for 1 h. In the middle of *in-situ* XAS measurement, *in-situ* XRD spectra was collected three times; after 5 and 120 min at 140 °C and after 60 min at 300 °C. XAS data processing was done with Athena/Artemis software included in the Demeter software package, based on FEFF6. The fitting was conducted by k² - weighted fits over the ranges indicated using a Hannings window (dk=0.5). Bond distance (R), Debye-Waller factor (σ^2) and energy shift (ΔE_0) were used to optimize the fitting results under the amplitude factor (S₀) of 0.9. Wavelet-transformed (WT) EXAFS was performed with the

Morlet function as a mother wavelet. κ and σ were set as 30 and 0.18, respectively, to improve the resolution of WT spectra.

H₂ TPR / CO₂ TPD / H₂-D₂ exchange Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) were conducted with a catalyst analyzer (BELCAT II, BEL Japan, Inc., Kyoto, Japan). In the case of H₂-TPR, the sample was pretreated in an Ar flow (30 mL min⁻¹) at 120 °C for 60 min and then cooled to 50 °C under the same gas condition. The gas was then switched to an Ar and H₂ mixed gas (19 mL min⁻¹ of Ar and 1 mL min⁻¹ of H₂) and the temperature was ramped up to 600 °C at a rate of 10 °C min⁻¹. The consumption of H₂ was monitored with a thermal conductivity detector (TCD) and mass spectrometer. In the case of CO₂-TPD, the sample was reduced in a H₂ flow (20 mL min⁻¹) for 60 min at the corresponding temperature and cooled to 50 °C under He flow (50 mL min⁻¹), and then exposed to a 10% CO₂/He flow (30 mL min⁻¹) for 90 min. The physisorbed CO₂ was removed by He flow (50 mL min⁻¹) at 25 °C for 30 min. The temperature was then increased up to 700 °C at a rate of 10 °C min⁻¹ under a He flow (20 mL min⁻¹). The desorbed CO₂ was monitored with a TCD and mass spectrometer. H₂-D₂ exchange study was conducted with 20 mg of catalyst. Pretreatments were carried out under 20 mL min⁻¹ of H₂ flow at applicable temperature for 5 h (140 and 180 °C) and 2 h (300 °C) and cooled to 25 °C. After pretreatments, the gas feed was switched to 15 % H₂ / 15 % D₂ / 70% Ar mixture (4 mL min⁻¹ H₂, 4 mL min⁻¹ D₂ and 18 mL min⁻¹ Ar), and the product distribution was evaluated by online mass spectrometry by monitoring $m/z = 2$ (H₂), 4 (D₂), 3 (HD) and 40 (Ar).

N₂ adsorption–desorption isotherms Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) and pore structure information of the materials were recorded via a BELSORP-max (MicrotracBEL Corp., Kyoto, Japan). after the sample pretreatment at 120 °C under vacuum for 6 h. The specific surface area (S_{BET}) and the total pore volume (V_{total}) were determined by using the N₂ adsorption isotherm data obtained at a temperature of -196 °C.

Thermogravimetric-differential thermal analysis Thermogravimetric-differential thermal analysis (TG-DTA) was performed under an H₂ and air atmosphere using a Rigaku Thermo Plus EVO II (Rigaku, Tokyo, Japan). Each 10 mg sample was loaded and heated at 120 °C for 60 min with an initial heating rate of 10 °C min⁻¹ under a 30 mL min⁻¹ N₂ flow to remove physisorbed water. Subsequently, the sample was cooled to 50 °C at a rate of 10 °C min⁻¹ and maintained at that temperature for 60 min under the same N₂ flow to allow the sample mass and temperature to stabilize. Next, the temperature ramped to 800 °C at a rate of 10 °C min⁻¹ under a 30 mL min⁻¹ of air an H₂ atomosphere, repectively.

Electron paramagnetic resonance Electron paramagnetic resonance (EPR) spectroscopy experiments were performed at 10 K using a JEOL FA200 X-band spectrometer (JEOL, Akishima, Japan). All EPR spectra were acquired under the spectrometer settings: microwave frequency, 9.0 GHz; center field, 330 mT; sweep width, 250 mT; modulation frequency, 100 kHz; sweep time, 4 min; modulation width, 1 mT; amplitude, 500; time constant, 0.3. Signal intensities were normalized to a MnO marker.

2. Ion-exchange of $\text{Na}_2\text{Ti}_3\text{O}_7$ to $\text{Ru}_x\text{Ti}_y\text{O}_z$

2.1. Ion-exchange properties with respect to NaHCO_3 concentration

pH is a most crucial factor that affects the ion-exchange process because the surface charge of an ion-exchange material varies depending on the pH⁴. The point of zero charge (PZC) of sodium titanate is known to be around pH 3.0 (Fig. S1)^{5,6}. At pH >3.0, the surface is negatively charged and facilitates ion-exchange as well as adsorption by the electrostatic attraction of cations. However, the pH of a solution containing $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was around pH 1.5-1.6 due to the hydrolysis reaction (Table S1). This acidic solution did not satisfy the conditions to attract Ru cations into the interlayer structure and instead caused Na^+ to be preferentially substituted by smaller radius H^+ rather than Ru cations⁶. Therefore, we used NaHCO_3 as a pH controller to optimize the ion-exchange of Na^+ to Ru cation. NaHCO_3 was utilized instead of NaOH to minimize the precipitation of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ to RuO_2 by an abrupt decrease of the local pH from a decrease in the high NaOH concentration.

$\text{Na}_2\text{Ti}_3\text{O}_7$ was ion-exchanged under four different conditions at 160 °C; without NaHCO_3 and with 0.02 M NaHCO_3 , 0.05 M NaHCO_3 , and 0.055 M NaHCO_3 . Table S1 shows the pH before and after the ion-exchange process. Without NaHCO_3 and at 0.02 M NaHCO_3 , highly acidic solutions (pH 1.9 and 2.38, respectively) were still maintained after the ion-exchange process, and the layered structure transformed into anatase (A- TiO_2) and rutile (R- TiO_2) because excess H^+ over the capacity of $\text{Na}_2\text{Ti}_3\text{O}_7$ was preferentially ion-exchanged with Na^+ , which exfoliated the layer structure to TiO_2 by dehydration at high temperature (Figs. S2, S3 and Table S1). However, titration of pH over 3, which was the condition over PZC, and a low concentration of H^+ due to the addition of 0.05 M NaHCO_3 facilitated the ion exchange to Ru ions and the layered structure was maintained after the ion-exchange process.

CO₂ methanation performance was evaluated after the ion-exchange process in a mixed feed gas (H₂/CO₂/N₂ = 71.25:23.75:5) at a flow rate of 20 mL min⁻¹ and 140 °C (Fig. S4). Without NaHCO₃ and with 0.02 M NaHCO₃, in which the layered structure was fully exfoliated, almost no activity was observed, whereas the 0.05 M and 0.055 M NaHCO₃ samples exhibited STYs that were tens of times higher and reached 0.0326 mol g_{cat}⁻¹ h⁻¹ for the 0.05 M NaHCO₃ sample. The decrease in activity to 0.0217 mol g_{cat}⁻¹ h⁻¹ for the sample with 0.055 M NaHCO₃ resulted from the trade off with the RuO₂ precipitate rather than ion exchange between the layered structure at over pH 5, which corresponded with the increase in the intensity of RuO₂ in the XRD patterns^{7,8}. Therefore, 0.05 M NaHCO₃ was selected as the optimum concentration for this study.

Table S1. pH before and after ion-exchange in difference NaHCO₃ concentrations.

pH	Without NaHCO ₃	NaHCO ₃ 0.02M	NaHCO ₃ 0.05M	NaHCO ₃ 0.055M
Before ion-exchange	1.59	1.95	3.05	5.02
After ion-exchange	1.90	2.38	7.02	7.03

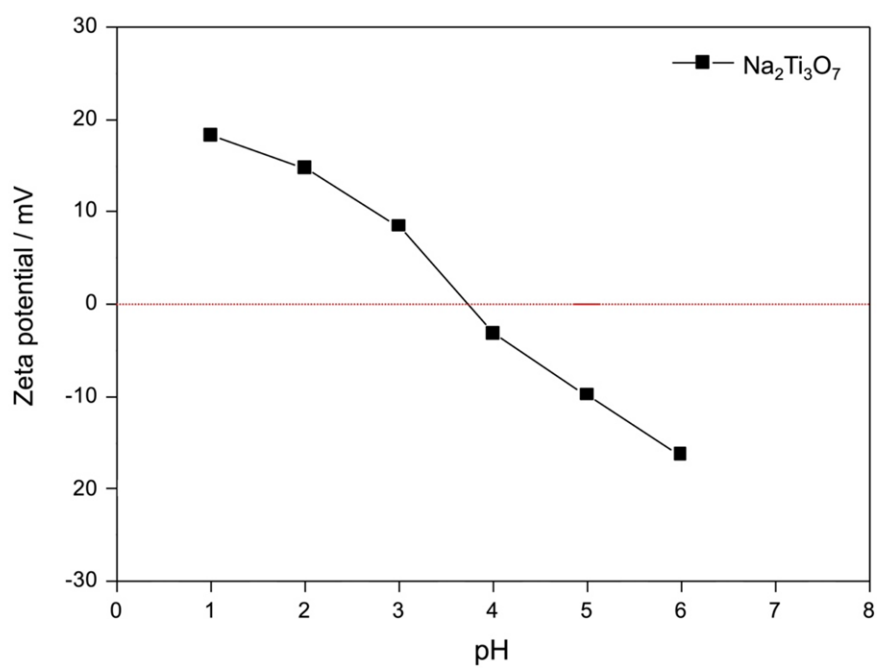


Figure S1. Zeta potential of $\text{Na}_2\text{Ti}_3\text{O}_7$.

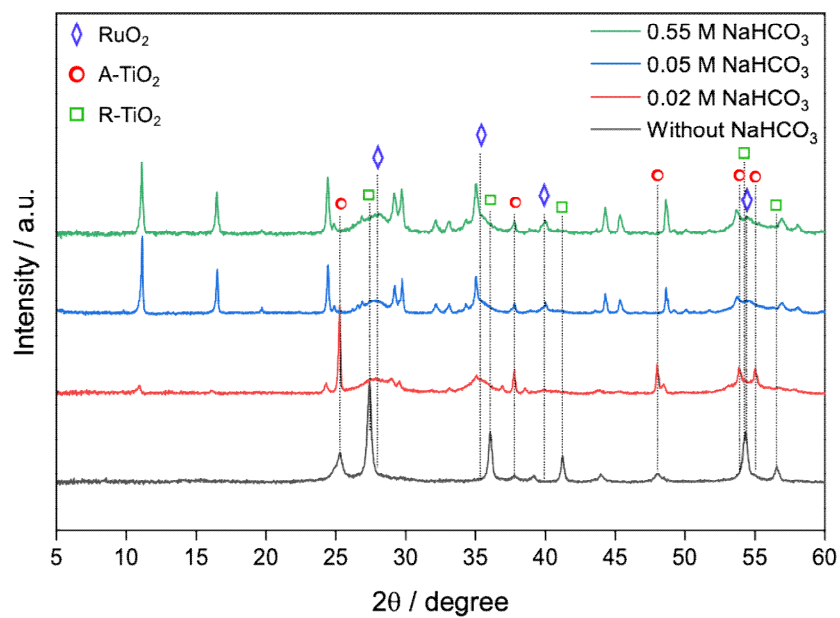


Figure S2. XRD spectra of ion-exchanged samples in the difference NaHCO_3 concentration.

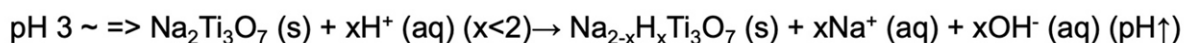
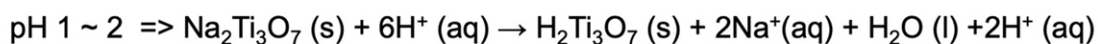
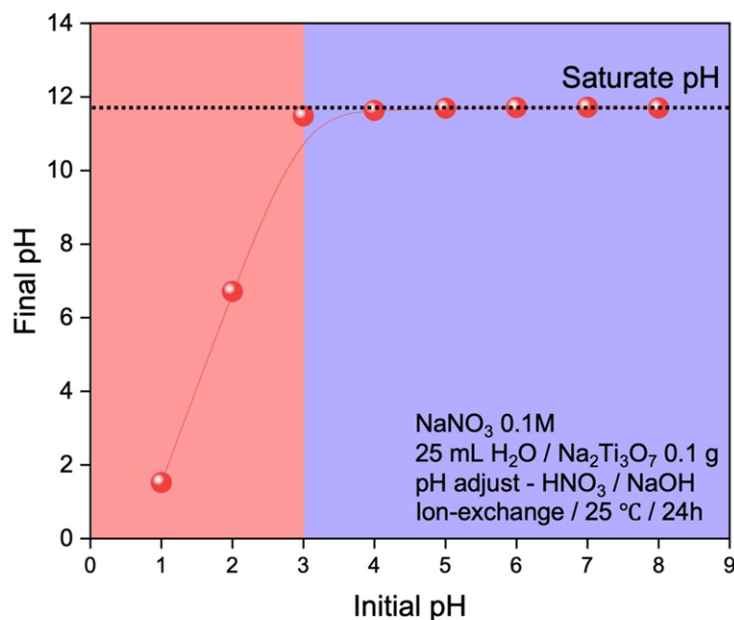


Figure S3. pH before and after ion-exchange in difference pH without Ru precursor. In pH 1~2 region, excessive H^+ still existed after ion-exchange process, whereas, from pH 3, $\text{Na}_2\text{Ti}_3\text{O}_7$ has enough capacity to uptake low concentration H^+ . Consequently, pH reached the saturated condition (~11.7) due to the hydroxyl ion (OH^-) attributed to hydrolysis of Na^+ . This result indicated that ion-exchange process should be proceed over ~ pH 3 otherwise excessive H^+ substitute Na^+ position rather than other target metal.

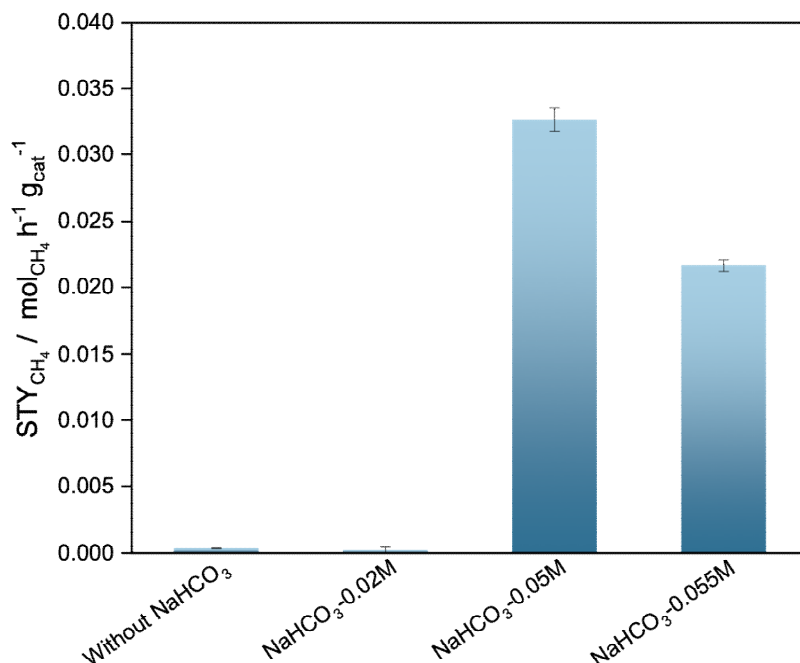


Figure S4. CO₂ methanation performance of Ion-exchanged samples in difference NaHCO₃ concentration. Reaction conditions: P = 0.1 MPa; Set temperature = 140 °C; H₂/CO₂/N₂ = 71.25/23.75/5; flow rate = 20 mL min⁻¹. Error bars represent the standard deviation of triplicate measurements for CO₂ methanation performance.

2.2. Ion-exchange properties with respect to temperature

The ion-exchange process of Na₂Ti₃O₇ is considered to be an endothermic process with a positive ΔH value, which implies the ion-exchange ability would be elevated with an increase in the exchange temperature⁴. Therefore, ion-exchange was conducted at various temperatures between 100 and 230 °C. After the ion-exchange process, the [200] plane that represents the interlayer distance was shifted to lower angle with an increase of the ion-exchange temperature and reached 11.14° at 160 °C (Fig. S5). The peak shift indicates shrinkage of the interlayer structure by the ion-exchange of Na⁺ (1.02 Å) to small radius Ru⁴⁺ (0.62 Å) and the 160 °C condition resulted in the largest amount of Ru uptake⁹. At over 160 °C, the [200] peak was shifted back to low angle

and completely disappeared at 230 °C with the emergence of strong A-TiO₂ peaks, which indicated destruction of the layered structure at this high ion-exchange temperature.

After the ion-exchange process, the CO₂ methanation performance was evaluated in a mixed feed gas (H₂/CO₂/N₂ = 71.25:23.75:5) at a flow rate of 20 mL min⁻¹ and 140 °C (Fig. S6). The catalytic performance of the ion-exchanged sample exhibited a gradual increase with the ion-exchange temperature, reaching a maximum of STY_{CH₄} of 0.033 mol g_{cat}⁻¹ h⁻¹ at 160 °C. However, an increase in the ion-exchange temperature beyond 160 °C resulted in a significant decline in activity with the STY_{CH₄} dropping to 0.005 mol g_{cat}⁻¹ h⁻¹ at 230 °C. These results exhibited a similar tendency to that observed in the amount of Ru uptake in the layer structure from XRD (Fig. S5). No product except CH₄ was confirmed by gas chromatography (GC) under all conditions. Therefore, 160 °C was selected as the optimum ion-exchange temperature.

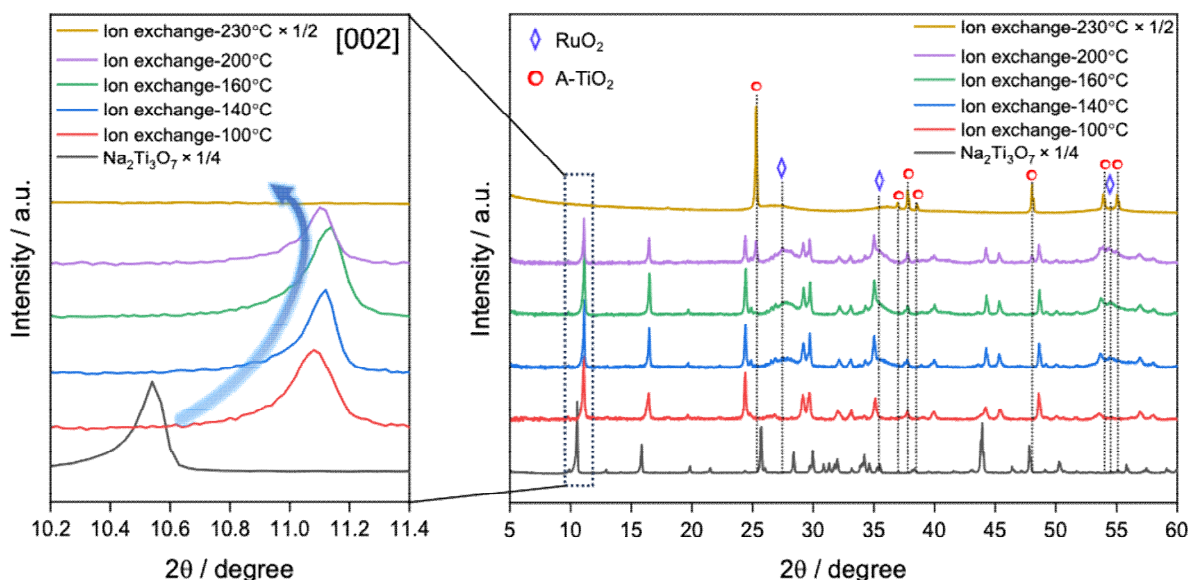


Figure S5. XRD Spectra of ion-exchanged samples in the difference temperature.

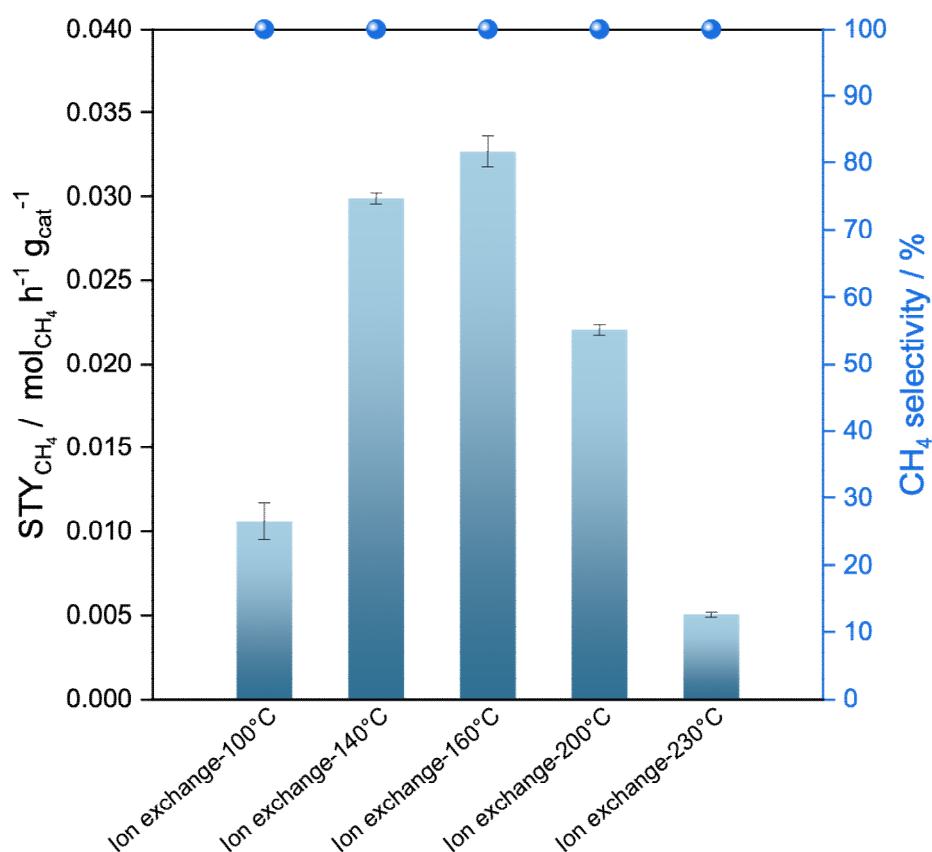


Figure S6. CO₂ methanation performance of Ion-exchanged sample in difference ion-exchange temperature. Reaction conditions: P = 0.1 MPa; Set temperature = 140 °C; H₂/CO₂/N₂ = 71.25/23.75/5; flow rate = 20 mL min⁻¹. Error bars represent the standard deviation of triplicate measurements for CO₂ methanation performance.

2.3. Ion-exchange properties with respect to RuCl₃·xH₂O concentration

Sufficient Ru precursor should be dissolved in the ion-exchange solution for the ion-exchange of Na₂Ti₃O₇ to Ru_xTi_yO_z with maximum Ru content. Moreover, the rate-determining step of ion-exchange is chemical interaction; therefore, an increase of the metal precursor concentration shortens the diffusion length between the metal cation and sodium titanate, which facilitates the ion-exchange process¹⁰. Therefore, the concentration of the Ru precursor, RuCl₃·xH₂O, was controlled with five different conditions (Table S3). Fig. S7 shows that the catalytic performance gradually

increased to around ca. 0.033 mol g_{cat}⁻¹ h⁻¹ with an increase in the amount of RuCl₃·xH₂O and was maintained at a similar level. The slight decline in the activity when the amount of RuCl₃·xH₂O exceeded 0.1442 g was expected due to an increase in the proportion of precipitated RuO₂ in the catalyst. Therefore, a concentration ratio of Ru/Na between 0.69 and 1.05 was the optimum condition for the ion-exchange of Na₂Ti₃O₇ to Ru_xTi_yO_z (Table S3). Considering aspects such as cost efficiency and commercialization of the catalyst, 0.11554 g of RuCl₃·xH₂O, which had an STY_{CH₄}/Ru precursor of 0.283 mol g_{cat}⁻¹ h⁻¹ g_{RuCl₃}⁻¹, was selected as the optimum condition.

Table S2. Calculated ion-exchange conditions with various precursor concentrations.

RuCl ₃ xH ₂ O (g)	0.0577	0.08655	0.1154	0.1442	0.1731
Ru amount (g) ¹	0.023 ~0.028	0.034~0.042	0.046~0.056	0.057~0.070	0.069~0.084
Ru amount (mmol)	0.23 ~0.28	0.34~0.42	0.46~0.56	0.57~0.70	0.68~0.84
Ru/Na ²	0.34 ~0.42	0.52~0.63	0.69~0.84	0.86~1.05	1.03~1.27

¹ RuCl₃·xH₂O (ReagentPlus ®, > 99.9%, Ru contents 40.00-49.00%)

² Na contents was determined by the amount of Na in 0.1 g of Na₂Ti₃O₇, 0.66 mmol

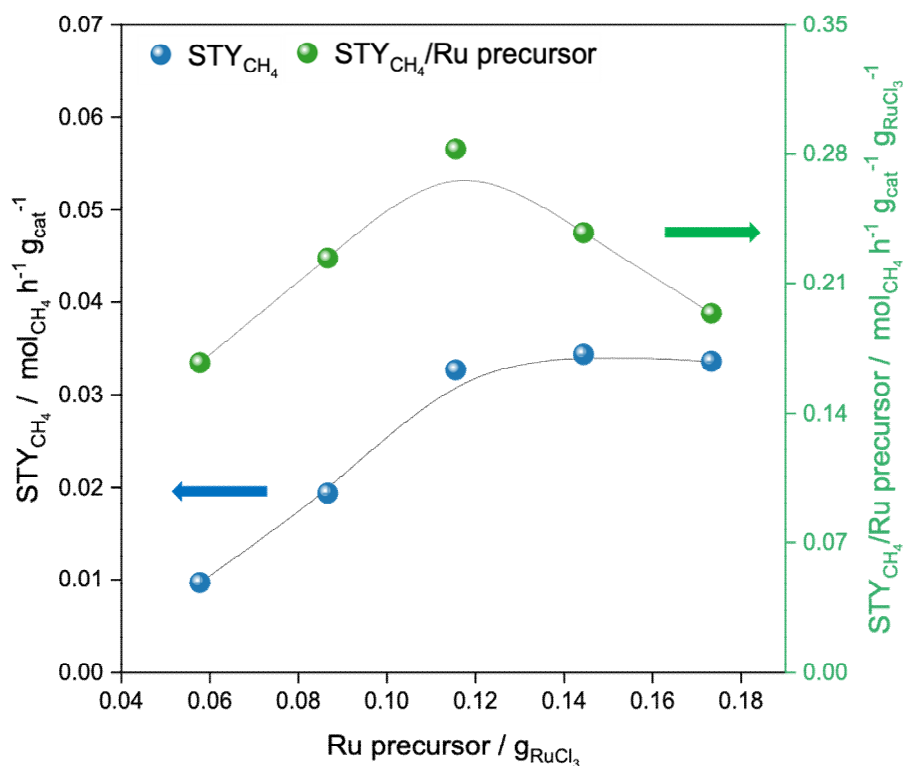


Figure S7. CO₂ methanation performance for ion-exchanged samples prepared with various precursor concentrations. Reaction conditions: P = 0.1 MPa; Set temperature = 140 °C; H₂/CO₂/N₂ = 71.25/23.75/5; flow rate = 20 mL min⁻¹.

3. Characterization of Fresh and Used Ru_xTi_yO_z

3.1. Characterization of fresh Ru_xTi_yO_z

Crystal structure of Ru_xTi_yO_z

To investigate the crystal structure of Ru_xTi_yO_z, Le Bail refinement was performed to obtain the lattice parameters (Fig. S8). Na₂Ti₃O₇ and H₂Ti₃O₇ were also refined by the Rietveld method as reference samples (Fig. S9). Table S3 shows that the space group of Ru_xTi_yO_z transformed into C2/m as H₂Ti₃O₇, and the unit cell of Ru_xTi_yO_z was significantly distorted both angularly and with respect to the length compared with the reference samples, which implied the existence of Ru within the interlayer structure. To clarify that this distortion was not attributed to H⁺ intercalation i.e., Na_xH_{2-x}Ti₃O₇, but

rather to Ru ion, $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ was prepared by ion-exchange $\text{Na}_2\text{Ti}_3\text{O}_7$ at pH 2 and pH 3 ($\text{Na}_2\text{Ti}_3\text{O}_7\text{-pH2}$ and $\text{Na}_2\text{Ti}_3\text{O}_7\text{-pH3}$). The pH of 25 mL of deionized water was set to 2 and 3, respectively, using 0.1 M HCl solution. 0.1 g of $\text{Na}_2\text{Ti}_3\text{O}_7$ was then added to the solution and hydrothermally treated with vigorous stirring at 160 °C for 24 h. After 24 h, the solution was cooled to room temperature and filtrated with sufficient water and dried at 100 °C for 6 h. Fig. S10 shows that there was a noticeable difference in the crystal structure between the $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ compound and $\text{Ru}_x\text{Ti}_y\text{O}_z$. In the case of the $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ compound, the shift to low angle was proportional to the degree of H^+ substitution for Na^+ due to the lattice shrinkage due to the smaller size of H^+ . In contrast, $\text{Ru}_x\text{Ti}_y\text{O}_z$ did not follow this tendency but instead revealed an unpredictable shift of angles, which indicated the different crystal structure of $\text{Ru}_x\text{Ti}_y\text{O}_z$ due to the Ru cation (Table S4).

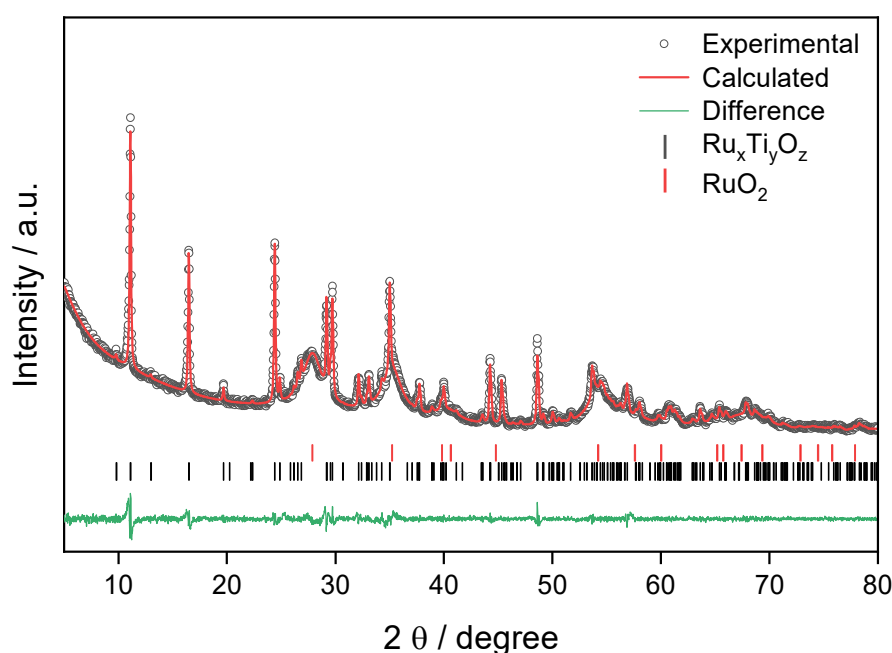


Figure S8. Le Bail refinement of $\text{Ru}_x\text{Ti}_y\text{O}_z$.

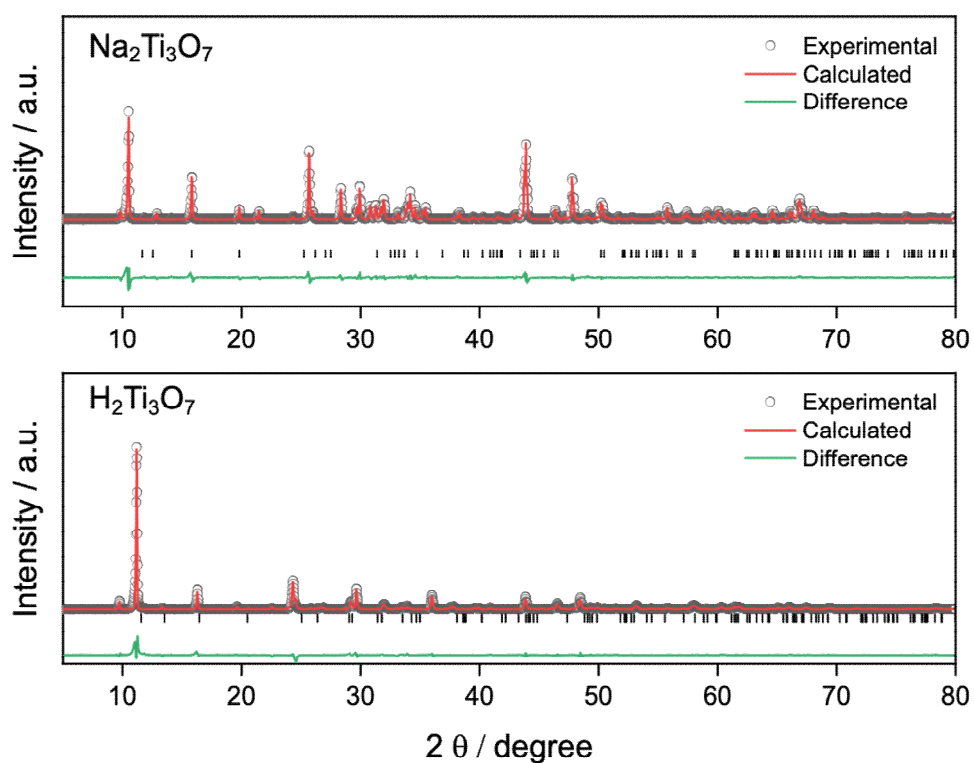


Figure S9. Rietveld refinement of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{H}_2\text{Ti}_3\text{O}_7$.

Table S3. Structural parameters for the $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Ru}_x\text{Ti}_y\text{O}_z$, and $\text{H}_2\text{Ti}_3\text{O}_7$

Sample	$\text{Na}_2\text{Ti}_3\text{O}_7$	$\text{Ru}_x\text{Ti}_y\text{O}_z$	$\text{H}_2\text{Ti}_3\text{O}_7$
Refinement	Rietveld	Le bail	Rietveld
Space group (Patterson)	P2/m	C2/m	C2/m
a	8.56262 ± 0.001	16.35080 ± 0.00007	16.0414 ± 0.0007
b	3.80214 ± 0.00005	3.74286 ± 0.000016	3.7526 ± 0.0001
c	9.12710 ± 0.0001	9.26628 ± 0.000035	9.1975 ± 0.0002
β	101.5970 ± 0.009	103.5407 ± 0.0037	101.433 ± 0.003

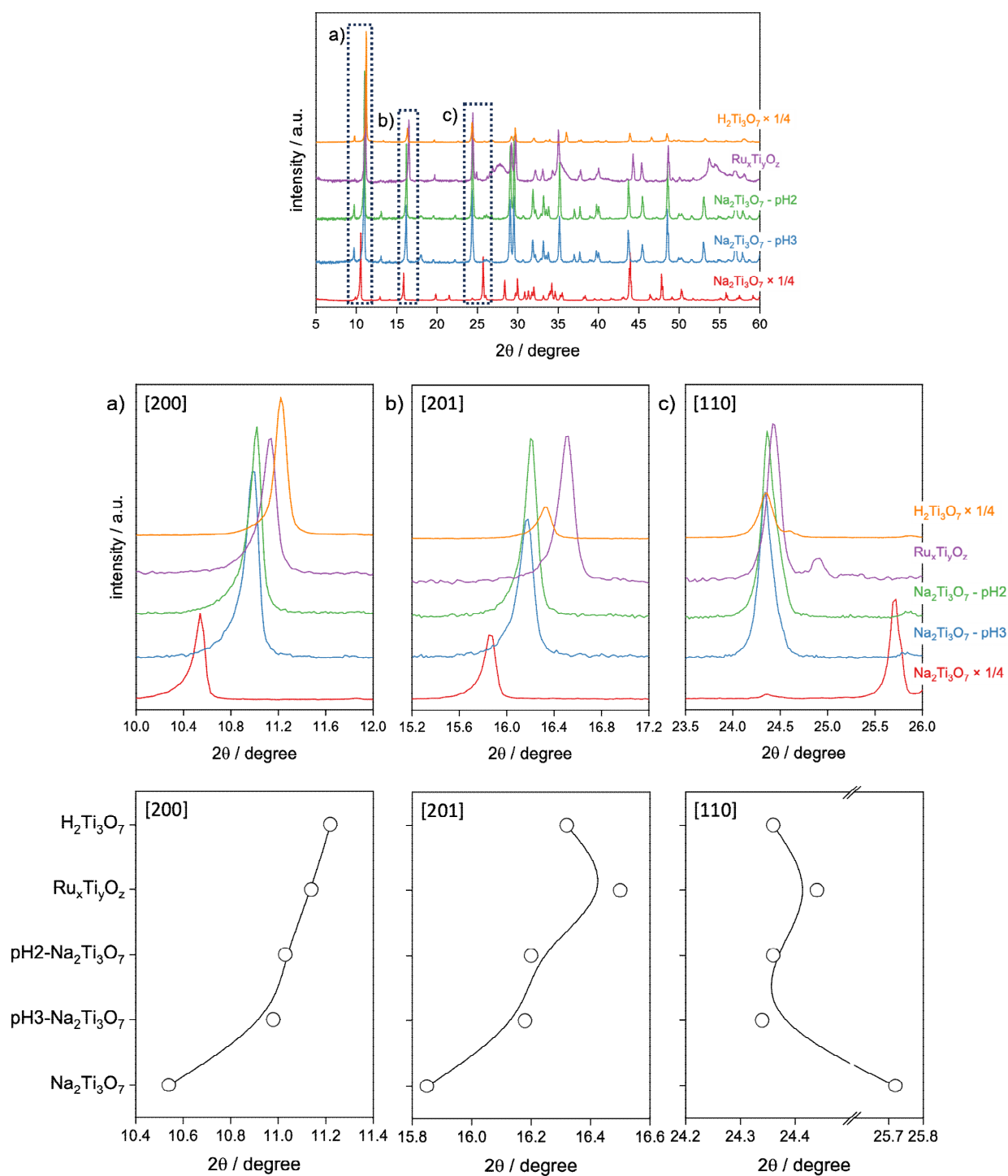


Figure S10. XRD spectra and peak positions of [200], [201] and [110] planes of $\text{Ru}_x\text{Ti}_y\text{O}_z$ and reference samples.

Table S4. Structural parameters for the $\text{Na}_2\text{Ti}_3\text{O}_7$ -pH2, $\text{Na}_2\text{Ti}_3\text{O}_7$ -pH3, and $\text{Ru}_x\text{Ti}_y\text{O}_z$ by Le bail refinement

Sample	$\text{Na}_2\text{Ti}_3\text{O}_7$ -pH2	$\text{Na}_2\text{Ti}_3\text{O}_7$ -pH3	$\text{Ru}_x\text{Ti}_y\text{O}_z$
Space group (Patterson)	C2/m	C2/m	C2/m
a	16.39074+-0.000039	16.38981+-0.00047	16.35080 ± 0.00007
b	3.746520+-0.000064	3.746551+-0.000077	3.74286 ± 0.000016
c	9.26907+-0.00017	9.26934+-0.00020	9.26628 ± 0.000035
β	102.1773+-0.0017	102.1608+-0.0020	103.5407 ± 0.0037

Morphologies of $\text{Ru}_x\text{Ti}_y\text{O}_z$

Figure S11 illustrates the scanning electron microscopy (SEM) images of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Ru}_x\text{Ti}_y\text{O}_z$. The large crystalized $\text{Na}_2\text{Ti}_3\text{O}_7$ became fine-particle size with irregular crystal size after ion exchange, as the hydrothermal ion exchange process and ion exchange from Na to Ru interrupted the highly ordered $\text{Na}_2\text{Ti}_3\text{O}_7$ crystal, resulting in the separation into fine crystal size. The particle size of $\text{Ru}_x\text{Ti}_y\text{O}_z$ exhibited a broad range between several nanometers and micrometers, as confirmed by STEM-EDS (Fig. S12-S15). In addition, ultra-fine RuO_2 was distributed in an aggregated form on the $\text{Ru}_x\text{Ti}_y\text{O}_z$ as an undesirable by-product (Fig. S11-S15). Table S6 demonstrated a significant increase in surface area and pore volume following ion exchange, which was mainly attributed to the nanoporous RuO_2 . Nevertheless, the preservation of a 20-fold higher surface area than $\text{Na}_2\text{Ti}_3\text{O}_7$ after reaction at 140 °C indicated that $\text{Na}_2\text{Ti}_3\text{O}_7$ was redistributed as fine size $\text{Ru}_x\text{Ti}_y\text{O}_z$ through ion-exchange, in accordance with the STEM images (Table S5 and Fig. S13-16).

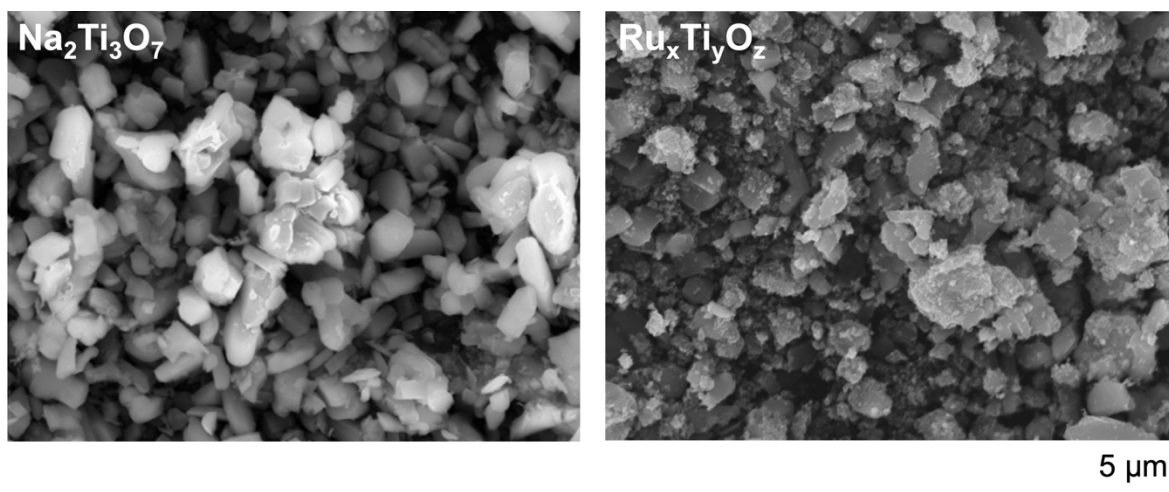


Figure S11. Morphology of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Ru}_x\text{Ti}_y\text{O}_z$ measured by SEM.

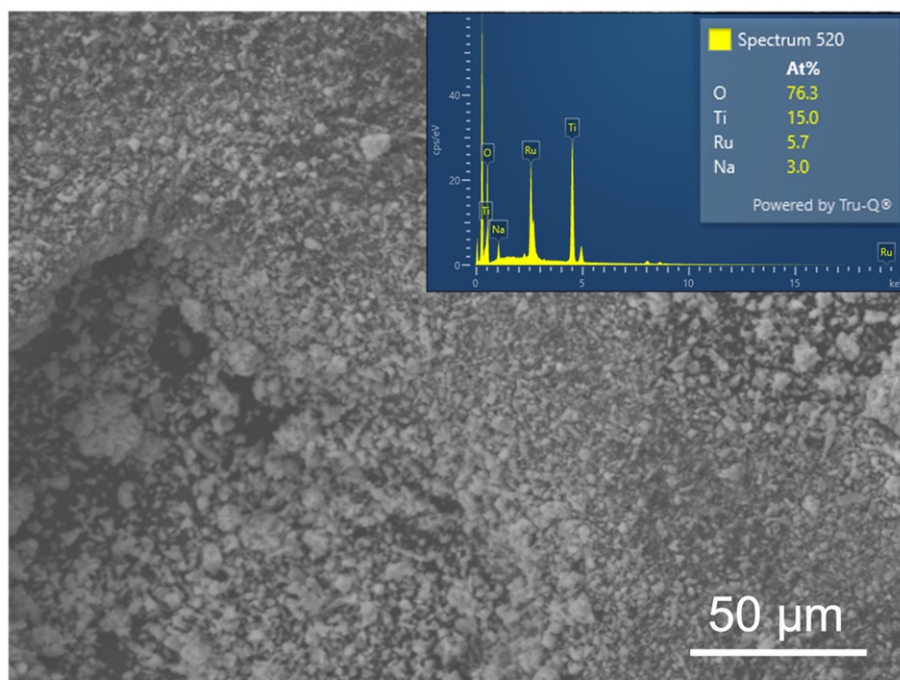


Figure S12. Morphology of $\text{Ru}_x\text{Ti}_y\text{O}_z$ measured in low magnification by SEM/EDS.

Table S5. BET surface area (S_{BET} , $\text{m}^2 \text{g}^{-1}$) and total pore volume (V_{total} , $\text{cm}^3 \text{g}^{-1}$) of $\text{Na}_2\text{Ti}_3\text{O}_7$, fresh $\text{Ru}_x\text{Ti}_y\text{O}_z$, and $\text{Ru}_x\text{Ti}_y\text{O}_z$ -140 °C-24h.

	$\text{Na}_2\text{Ti}_3\text{O}_7$	$\text{Ru}_x\text{Ti}_y\text{O}_z$	$\text{Ru}_x\text{Ti}_y\text{O}_z$ -140°C-24h
Surface area ($\text{m}^2 \text{g}^{-1}$)	1.02	97.29	20.17
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.0107	0.1120	0.0316

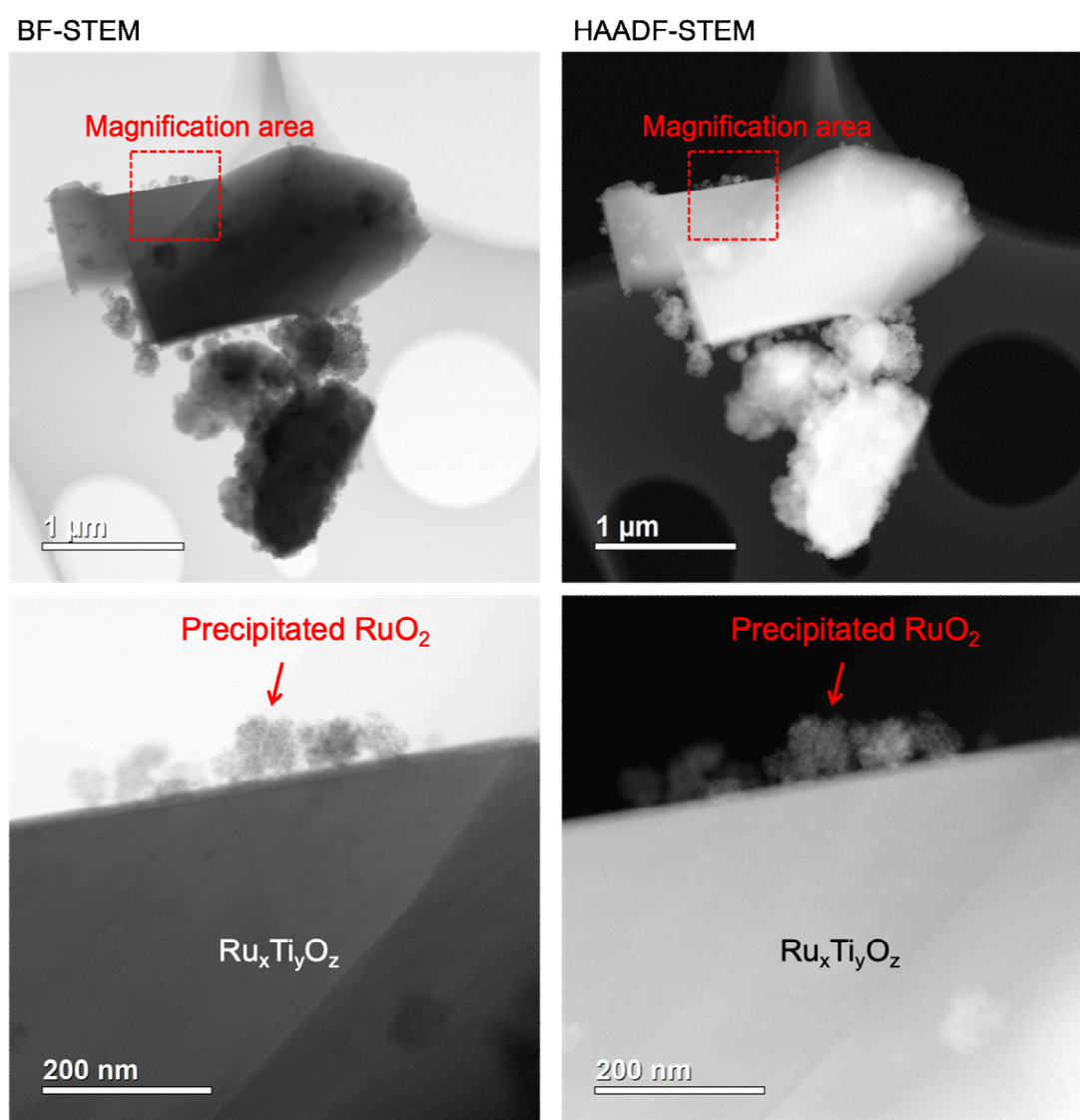


Figure S13. BF and HAADF-STEM images fresh $\text{Ru}_x\text{Ti}_y\text{O}_z$ with low magnification.

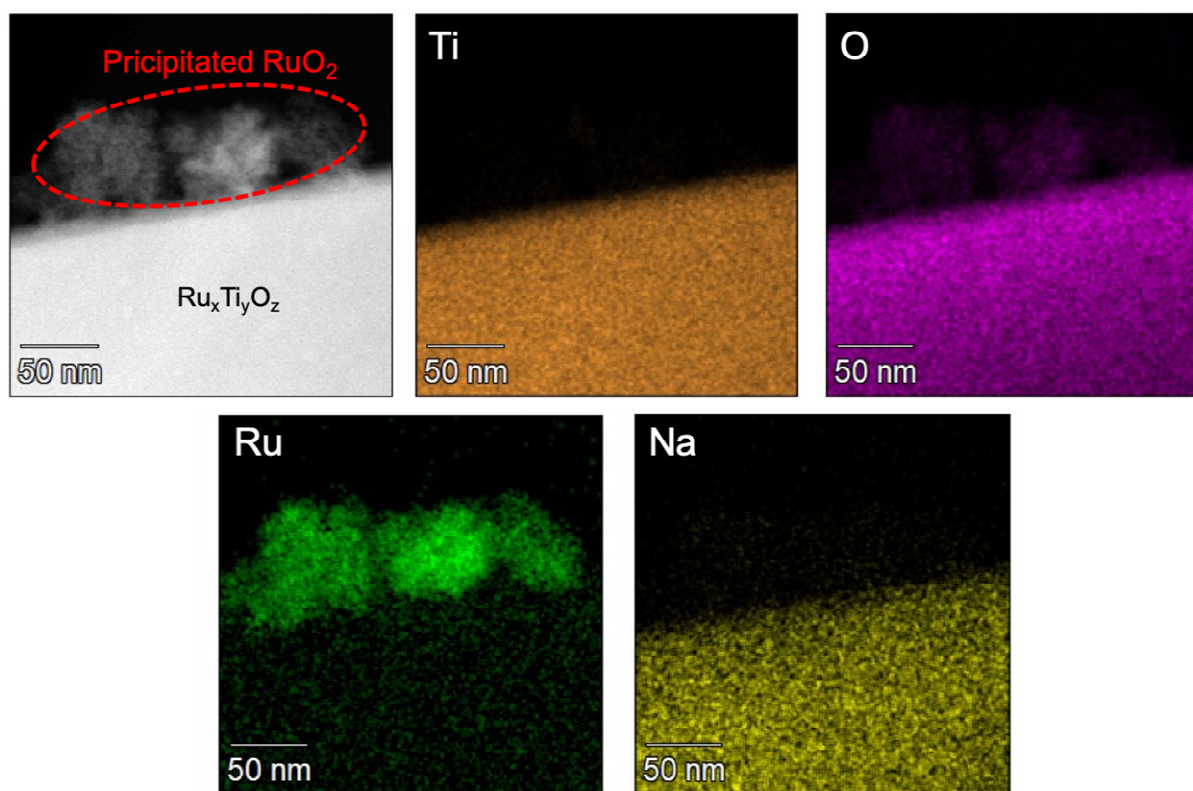


Figure S14. HAADF-STEM and EDS images fresh $\text{Ru}_x\text{Ti}_y\text{O}_z$ with low magnificant.

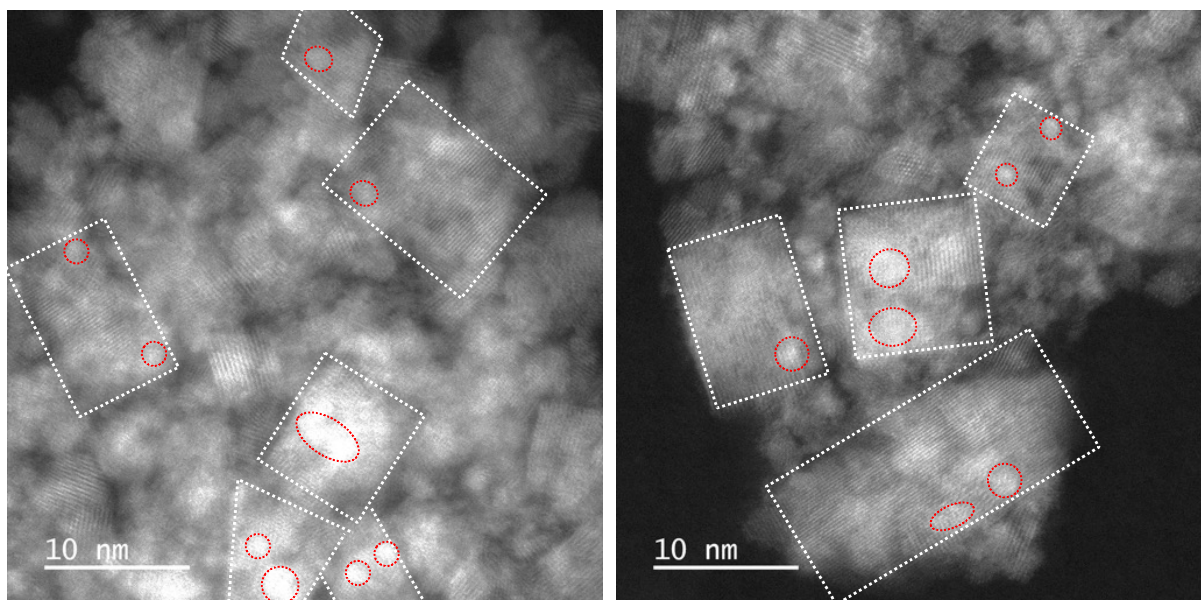


Figure S15. High magnification HAADF-STEM images of fresh $\text{Ru}_x\text{Ti}_y\text{O}_z$. The morphology of $\text{Ru}_x\text{Ti}_y\text{O}_z$ consisted of a mixture of precipitated RuO_2 and crystallized $\text{Ru}_x\text{Ti}_y\text{O}_z$. (White : $\text{Ru}_x\text{Ti}_y\text{O}_z$, Red : precipitated RuO_2).

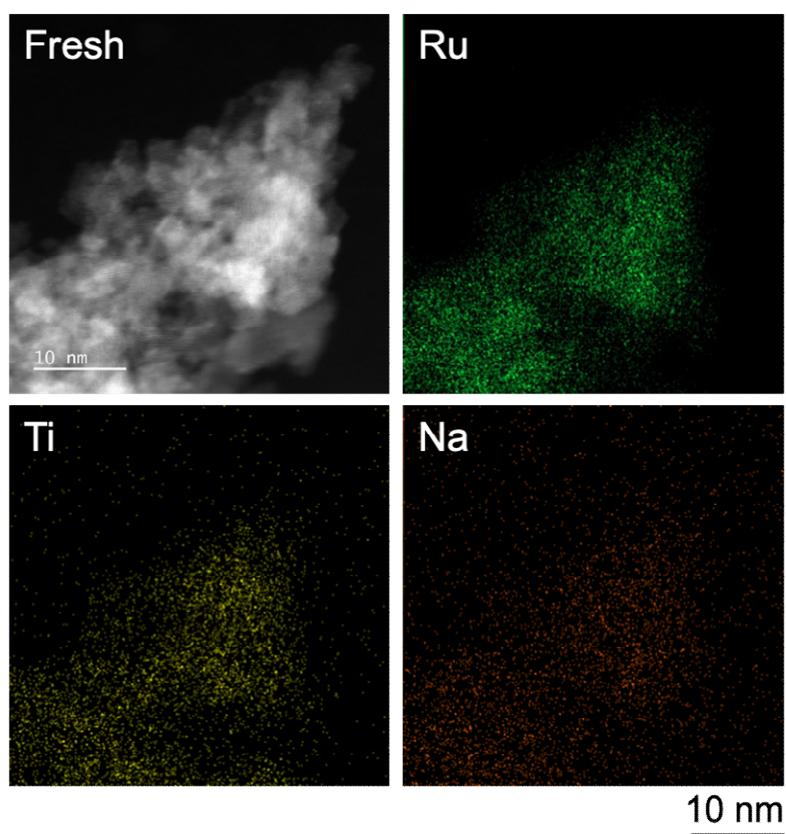


Figure S16. High magnification HAADF-STEM and EDS images fresh $\text{Ru}_x\text{Ti}_y\text{O}_z$.

Local structure of $\text{Ru}_x\text{Ti}_y\text{O}_z$

$\text{RuO}_2\text{-pH7}$ was prepared to distinguish the local structure between $\text{Ru}_x\text{Ti}_y\text{O}_z$ and precipitated RuO_2 . Fig. S17 showed that $\text{RuO}_2\text{-pH7}$ had a similar form of hydrate RuO_2 ($\text{RuO}_2 \cdot 0.29\text{H}_2\text{O}$) which had comparable nearest Ru-O octahedral environments with $\text{Ru}_x\text{Ti}_y\text{O}_z$ ¹¹. However, the phase shift and increase in the intensity compare with $\text{Ru}_x\text{Ti}_y\text{O}_z$ between 2~3.5 Å, implying that existence of additional scattering Ru-O-Ti path mostly from adsorbed and interlayer Ru species with layered $(\text{Ti}_3\text{O}_7)^{2-}$ ¹². The weak signal of second shell signal was due to disordered structure of intercalated Ru and multi scattering path length between Ru^{4+} and distorted $(\text{Ti}_3\text{O}_7)^{2-}$ ^{13–15}. Moreover, Ti K-edge XAS spectra also collected to investigate the local structure of Ti species. After ion-exchange process, there was no significant variation on the oxidation state of

Ti and maintained around Ti^{4+} oxidation state as $\text{Na}_2\text{Ti}_3\text{O}_7$ (Fig. S18a). The Ti pre-K-edge representing Ti-O polyhedral structure showed the strong A2 peak, which is mostly observed in the layered titanate, at $\text{Ru}_x\text{Ti}_y\text{O}_z$, indicating well preserve of layered geometric structure at $\text{Ru}_x\text{Ti}_y\text{O}_z$. Fig. S18c and S18d also showed that difference oscillation with additional peaks at the high k value ($6 \text{ \AA}^{-1} \sim$) in k-space EXAFS spectra and asymmetric oscillation between $2.2 \sim 3.5 \text{ \AA}$ due to the contribution of Ru scattering path, implying the existence Ti-O-Ru path as well as Ti-O-Ti path¹⁶.

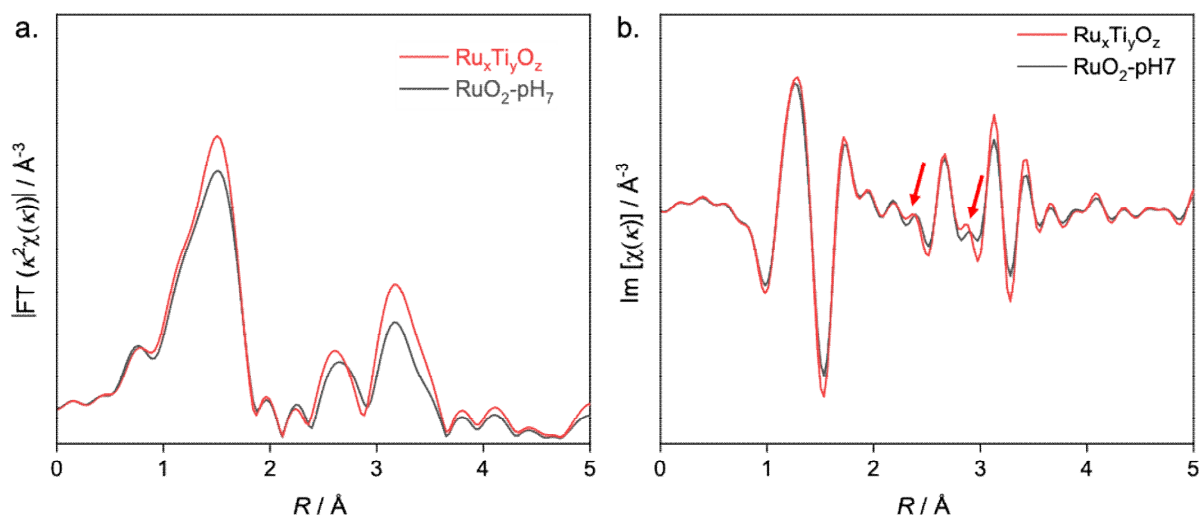


Figure S17. Fourier-transform(FT) EXAFS part of the Fourier transform results of $\text{RuO}_2\text{-pH}_7$ and $\text{Ru}_x\text{Ti}_y\text{O}_z$ with k^2 weighting; a, magnitude part. b, imaginary part.

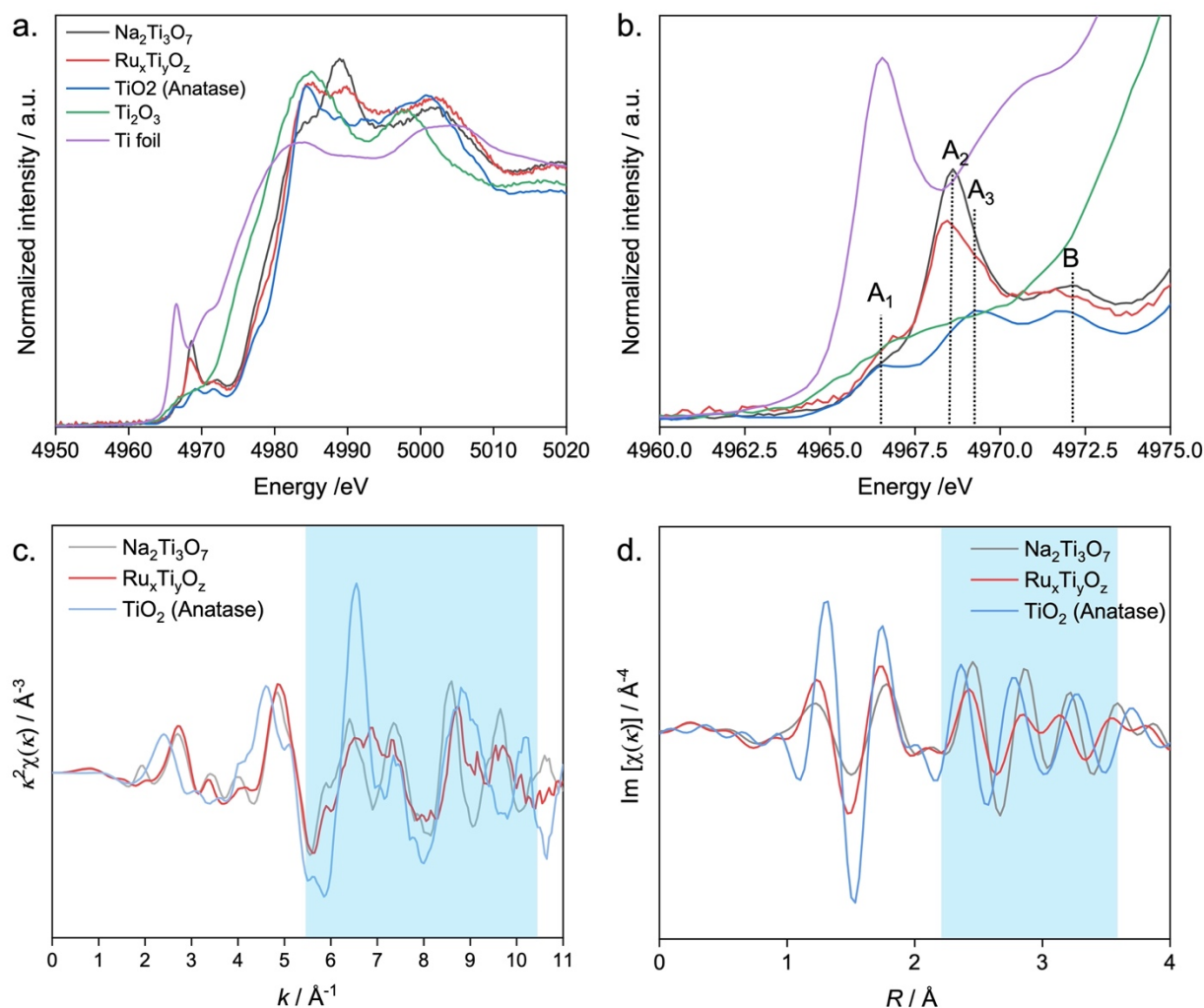


Figure S18. a, Ti K-edge XANES spectra of Ti references and $\text{Ru}_x\text{Ti}_y\text{O}_z$. b, pre-edge features of Ti K-edge XANES spectra of Ti references and $\text{Ru}_x\text{Ti}_y\text{O}_z$. The A_1 pre-peak is attributed to a triply degenerate (t_{2g}) level transition, while the A_2 and A_3 pre-peak are due to a doubly degenerate (e_g) level transition. B is assigned to the transition between the 1s and 4p orbitals^{17,18}. c, k^3 -weighted $\chi(k)$ EXAFS data of Ti references and $\text{Ru}_x\text{Ti}_y\text{O}_z$. d, FT-EXAFS spectra of imaginary part of Ti references and $\text{Ru}_x\text{Ti}_y\text{O}_z$.

3.2. Importance of layered structure of $\text{Ru}_x\text{Ti}_y\text{O}_z$

It was demonstrated that the catalytic performance substantially diminished following the exposure of the catalyst at 300 °C (Fig. 3c). Figure S19 also illustrated that the catalyst was deactivated by 19.8% after exposure at 300 °C for 5 h, in contrast to the results of the 140 and 180 °C stability tests, indicating that the catalyst's physiochemical properties after exposure at 300 °C underwent a change. Consequently, XRD spectra of the used samples were also obtained in order to investigate the transformation of the structure at each reaction temperature (Fig. S20). At 140 °C, the layered structure of $\text{Ru}_x\text{Ti}_y\text{O}_z$ was well maintained, with the disappearance of RuO_2 and the emergence of metallic Ru peaks. By increasing the temperature to 180 °C and 300 °C, the layered structure started to distort and at 300 °C it mostly diminished, leaving a TiO_2 (B)-like structure and single strong metallic Ru peaks, indicating the collapse of the layered structure by the reduction of oxidic Ru species (Fig. S21)¹⁹.

To elucidate the relationship between the layered structure of $\text{Ru}_x\text{Ti}_y\text{O}_z$ and catalytic activity, the catalyst was subjected to exfoliation at 300, 500, and 800 °C in an N_2 environment, which were selected by TGA result (Fig. S22). Figure S23 illustrates that the layered structure was largely exfoliated and separated into TiO_2 and RuO_2 from 500 °C, accompanied by a significant decline in catalytic activity (90% ~) as the layered structure underwent exfoliation (Figure 3d). Moreover, the catalyst treated under 300 °C in unreducible (N_2) and reducible (reaction condition) exhibited deactivation rates of 55 % and 81 %, respectively. This implies that the ionic Ru with the layer (Ti_3O_7)²⁻ was of critical importance in the catalytic CO_2 methanation process (Fig. S24). To ascertain the critical role of the ionic Ru with the layered structure in the catalytic performance, we synthesized multiple reference catalysts (Fig. S25). With TiO_2 sample, which substituted the $\text{Na}_2\text{Ti}_3\text{O}_7$ to TiO_2 during the synthesis process, exhibited a

markedly low activity, even with the same amount of Ru. To confirm the activity of precipitated RuO_2 , we also synthesized RuO_2 -pH No adjust and RuO_2 -pH7 without adding $\text{Na}_2\text{Ti}_3\text{O}_7$ during the synthesis process. Even though an increase in pH resulted in a slight enhancement in activity, the observed STY_{CH_4} value was $\sim 0.003 \text{ mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$, which remained extremely low. Furthermore, a physical mixture of RuO_2 and $\text{Na}_2\text{Ti}_3\text{O}_7$ with the same amount of Ru as $\text{Ru}_x\text{Ti}_y\text{O}_z$ was prepared as a further reference sample, also showing an incomparably lower activity than $\text{Ru}_x\text{Ti}_y\text{O}_z$.

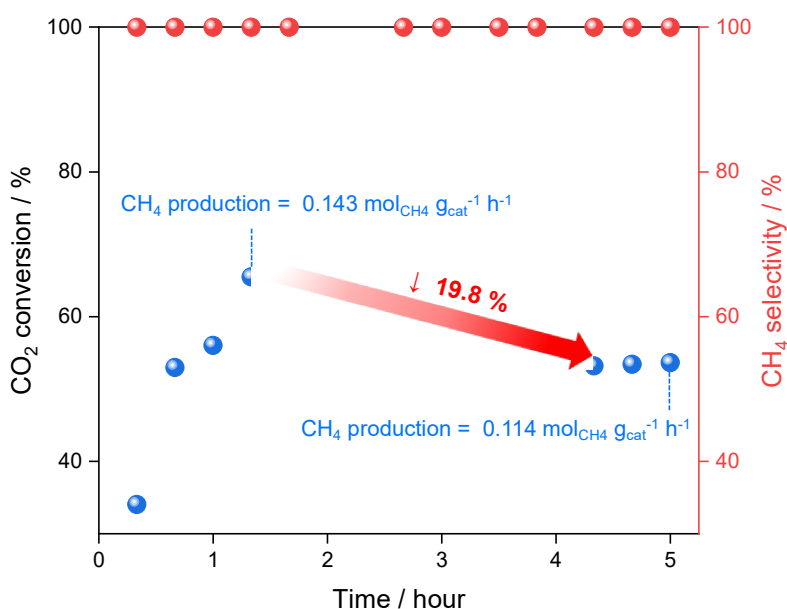


Figure S19. Stability test of $\text{Ru}_x\text{Ti}_y\text{O}_z$ at set temperature 300 °C. Reaction condition: $P = 1 \text{ bar}$, $\text{GHSV} = 24000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$.

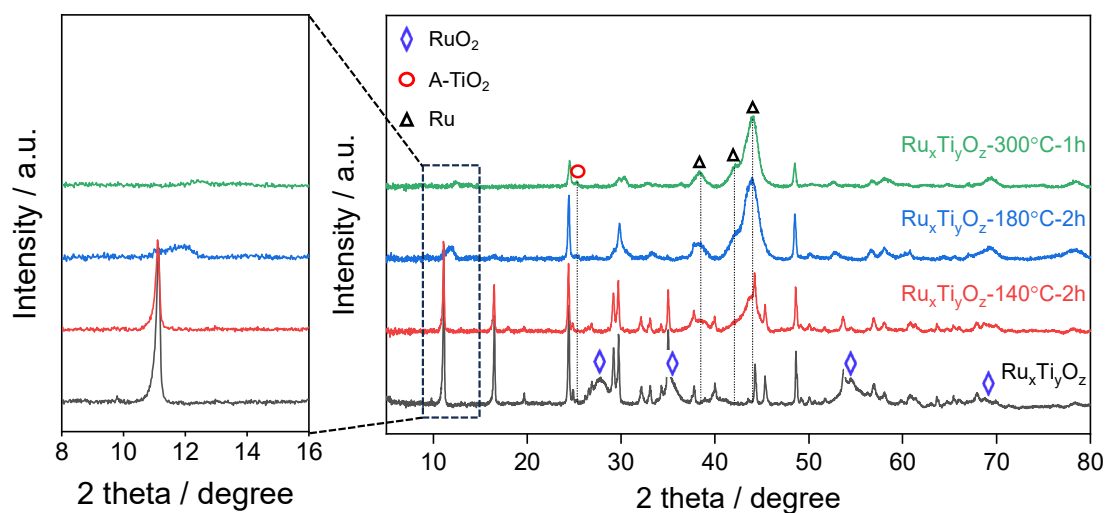


Figure S20. X-ray diffraction (XRD) spectra of used $\text{Ru}_x\text{Ti}_y\text{O}_z$ samples at 140, 180, and 300 °C.

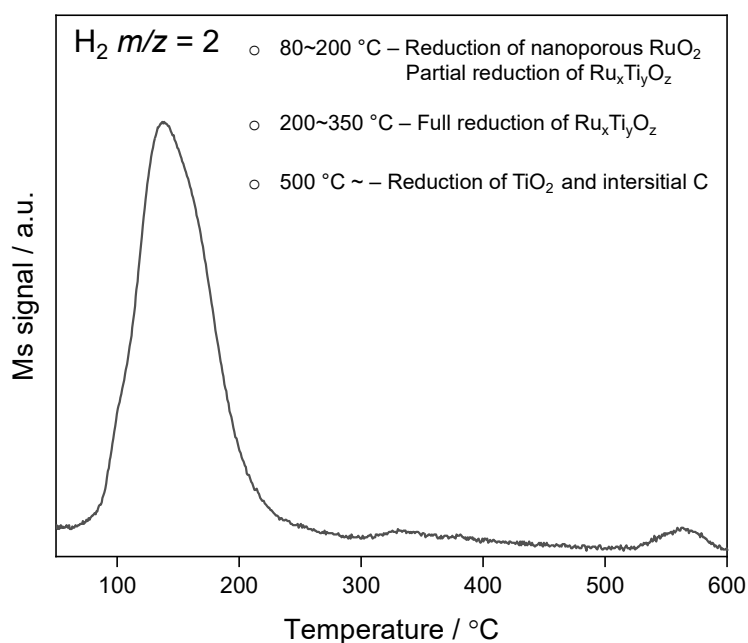


Figure S21. H_2 -TPR spectra of $\text{Ru}_x\text{Ti}_y\text{O}_z$. Asymmetric strong peaks between 80 ~ 200 °C indicated reduction of highly reducible nanoporous RuO_2 and partial reduction of $\text{Ru}_x\text{Ti}_y\text{O}_z$, fully reduced to metallic Ru between 200 ~ 350 °C region^{20–22}. The reduction peak over 500 °C was attributed to reduction of TiO_2 and reaction with interstitial carbon derived from exfoliation and recrystallization of $\text{Na}_2\text{Ti}_3\text{O}_7$ to TiO_2 ²³.

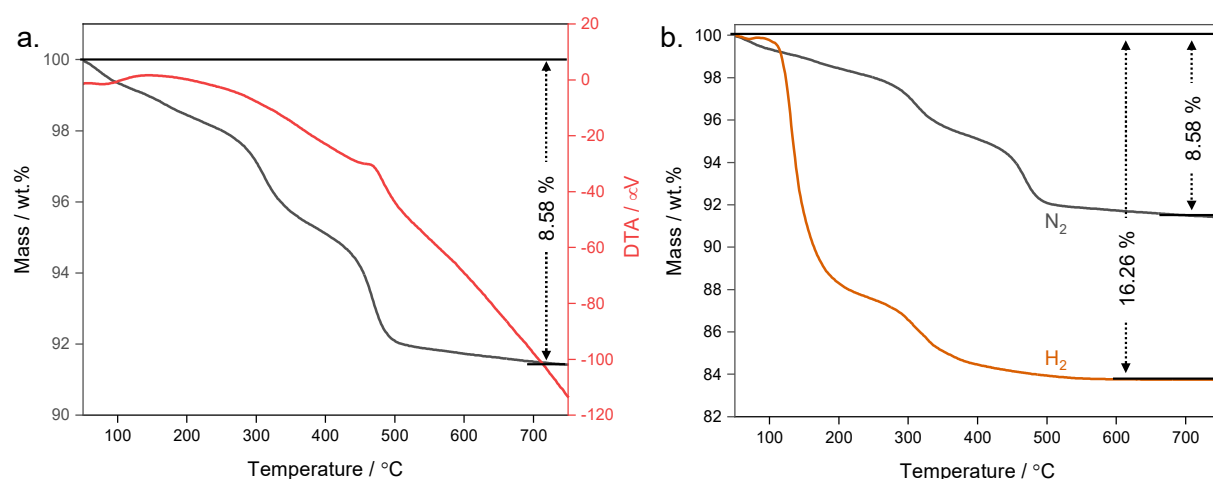


Figure S22. a, Thermogravimetric-differential thermal analysis (TG-DTA) plot of $\text{Ru}_x\text{Ti}_y\text{O}_z$ in N_2 condition. b, TG plot of $\text{Ru}_x\text{Ti}_y\text{O}_z$ in N_2 and H_2 condition. In the TG-DTA results of the N_2 condition, two significant weight losses were confirmed at approximately 300 and 500 $^{\circ}\text{C}$. At 300 $^{\circ}\text{C}$, the high temperature caused the unstable layer structure of $\text{Ru}_x\text{Ti}_y\text{O}_z$ to slip into a $\text{Na}_2\text{Ti}_6\text{O}_{13}$ -like structure, accompanied by dehydration, resulting in a weight loss of approximately 2 wt.% (Fig. S19). Subsequently, at approximately 500 $^{\circ}\text{C}$, a weight loss of 2–3 wt% was observed, accompanied by an exothermic peak, indicating the exfoliation of the layered structure and the crystallization of TiO_2 , which was observed by the XRD spectra (Fig. S23)²⁴. Furthermore, the amount of precipitated RuO_2 in the catalyst was estimated using the weight difference between N_2 -TG and H_2 -TG, assuming 31.89 wt.% of precipitated RuO_2 was included at $\text{Ru}_x\text{Ti}_y\text{O}_z$ catalyst.

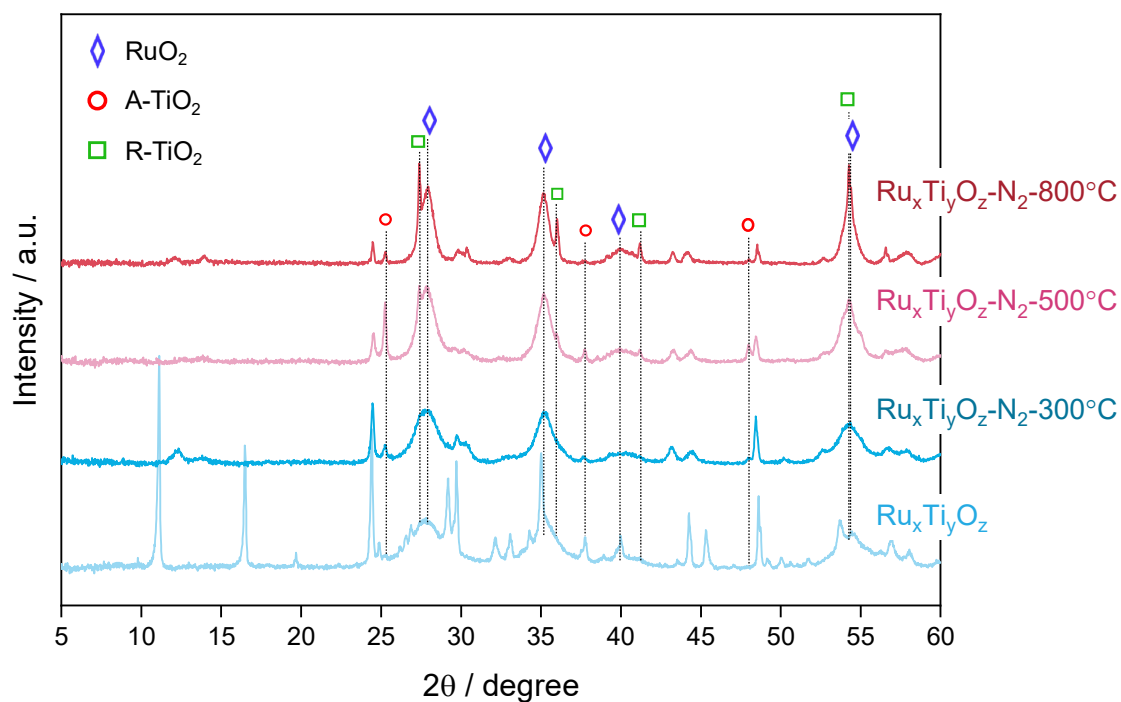


Figure S23. X-ray diffraction (XRD) spectra of $\text{Ru}_x\text{Ti}_y\text{O}_z$ samples after annealing at 300 °C, 500 °C, and 800 °C in N_2 .

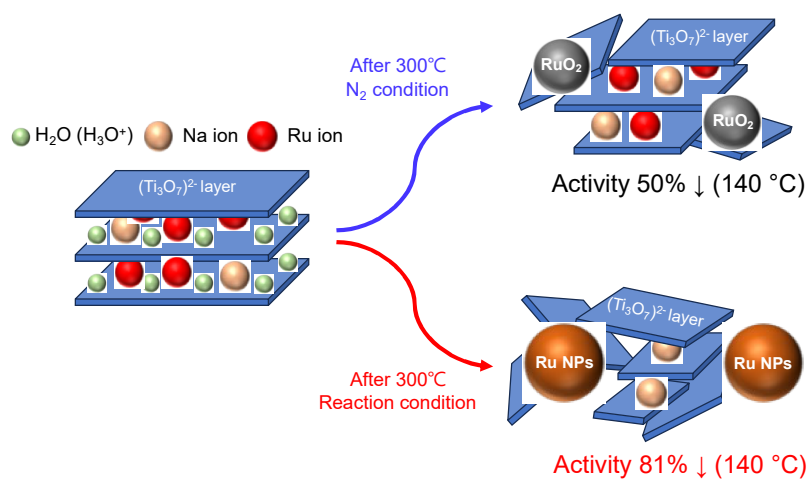


Figure S24. Schematic illustration of $\text{Ru}_x\text{Ti}_y\text{O}_z$ structural variation after exposure in different condition.

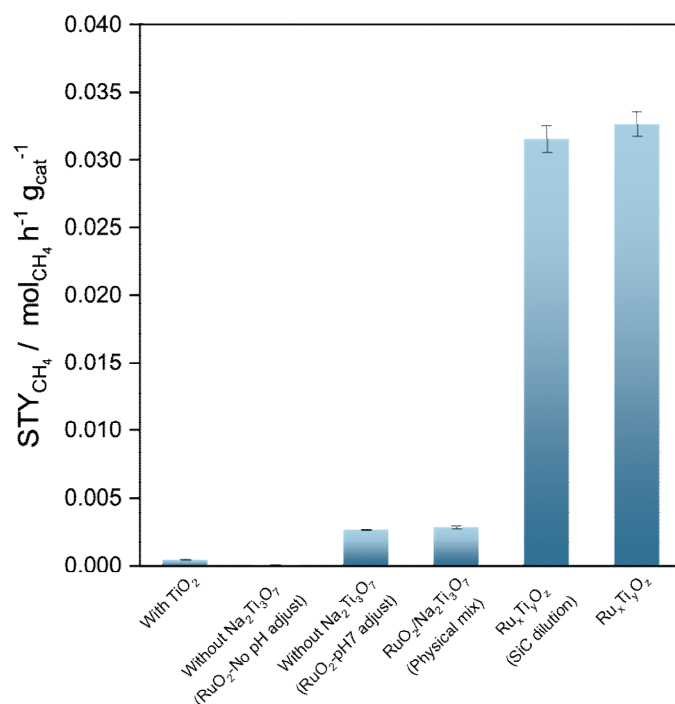


Figure. S25. CO₂ methanation performance with diverse reference catalyst substitutes Na₂Ti₃O₇ and diluted Ru_xTi_yO_z in SiC (1:25). All reference samples showed no CO₂ methanation ability at low temperature. Moreover, Ru_xTi_yO_z exhibited a high catalytic performance after diluting with SiC, illustrating the activity was not masked by hot spots. Reaction condition: Set temperature = 140 °C, $P = 1$ bar, GHSV = 24000 mL g_{cat}⁻¹ h⁻¹. Error bars represent the standard deviation of triplicate measurements for CO₂ methanation performance.

Table S6. State-of-the-art thermal catalysts for CO₂ methanation reported in recent literature.

Catalysts	Reaction condition	H ₂ :CO ₂	Pressure (bar)	Set temperature (°C)	GHSV or WHSV (mL h ⁻¹ g _{cat} ⁻¹)	CO ₂ conversion (%)	CH ₄ selectivity (%)	STY (mol _{CH₄} h ⁻¹ g _{cat} ⁻¹)	Ref.
Ru _x Ti _y O _z	50 mg 20 mL min ⁻¹ 23.8 % CO ₂	3:1	1	140 *Catalyst temperature: 142 °C	24,000 mL h ⁻¹ g _{cat} ⁻¹	14	100	0.0326	<i>This work</i>
				180 *Catalyst temperature: 194 °C		59.8	99.9 ~	0.139	
RuO _x Cy@C	260 mg 100 mL min ⁻¹ 23.8 % CO ₂	3:1	20	180	24,000 h ⁻¹	50	99.8	0.11	² <i>Nat. Mater.</i> 2023
Ru _{0.88} Co _{0.12} /TiO ₂	50 mg 20 mL min ⁻¹ 20 % CO ₂	4:1	1	250	24,000 mL h ⁻¹ g _{cat} ⁻¹	-	-	0.05	²³ <i>ACS nano</i> 2024
Ru/TiO ₂ (4 wt%)	50 mg 20 mL min ⁻¹ 15 % CO ₂	4:1	1	300	12,000 mL h ⁻¹ g _{cat} ⁻¹	89.2	98 ~	0.18	²⁵ <i>Nat. Commun.</i> 2022.
CeAlO _x /Ni/Ni foam	18 % CO ₂	4:1	1	240	10,000 h ⁻¹	~ 90	99.9 ~	-	²⁶ <i>Nat. Commun.</i> 2024

Ru/Ce _{0.9} Cr _{0.1} O _x (2.86 wt%)	20 % CO ₂	4:1	1	230	36000 mL h ⁻¹ g _{cat} ⁻¹	~ 10	100	-	²⁷ <i>ACS Catal.</i> 2021
Ru ₁ Ni/CeO ₂ (5 wt%)	100 mg 50 mL min ⁻¹ 18 % CO ₂	4:1	1	225	30,000 mL h ⁻¹ g _{cat} ⁻¹	~ 15	~ 95	~ 0.099	²⁸ <i>Appl. Catal. B</i> 2023
Ru/TiO ₂ (0.9 wt%)	20 mg 40 mL min ⁻¹ 20 % CO ₂	4:1	1	200	120,000 mL h ⁻¹ g _{cat} ⁻¹	~ 14	~ 100	-	²⁹ <i>iScience</i> 2022
Ru/MoO ₃ (1.9 wt%)	50 mg 8.3 mL min ⁻¹ 3 % CO ₂	3:1	1	250	10,000 mL h ⁻¹ g _{cat} ⁻¹	13.5	99.9 ~	0.0016	³⁰ <i>JACS</i> 2022
Ru@C-EDTA (28 wt%)	210 mg 23.8 % CO ₂	3:1	1	160	21,428 h ⁻¹	4.6	100	0.013	³¹ <i>JACS</i> 2019
Ru/CeO ₂ (5 wt%)	20 mg 50 mL min ⁻¹ 4.6 % CO ₂	4.8:1	1	300	7,640 h ⁻¹	83	99	0.232	³² <i>Appl. Catal. B</i> 2017
Ru/r-TiO ₂ (2.35 ~2.60 wt%)	200 mg 20 mL min ⁻¹ 10 % CO ₂	4:1	1	200	6,000 mL h ⁻¹ g _{cat} ⁻¹	27.4	~ 100	0.009	¹ <i>Catal. Sci. Technol.</i> 2016

Ru/Al ₂ O ₃ (5 wt%, 12 nm)	500 mg 13.3 % CO ₂	5:1	1	350	10,000	80	99.9	0.17	³³ Catal. Today 2020
Ru/Al ₂ O ₃ (2.3 wt%)	41.6 mL min ⁻¹ CO ₂ 15.5 %	5.2:1	1	350	28,000	61	~ 100	0.29	³⁴ Angew. Chem 2020
Ru/Na-TiO ₂ (5 wt%)	100 mg 150 mL min ⁻¹ CO ₂ 5 %	4:1	1	300	90,000	80	~ 100	0.44	³⁵ Appl. Catal. B 2017
Ru/r-TiO ₂ (5 wt%, 1.1 nm)	40 mg 50 mL min ⁻¹ CO ₂ 18 %	4:1	1	300	75,000 mL h ⁻¹ g _{cat} ⁻¹	65	~ 100	0.43	³⁶ Catal. Sci. Technol. 2014
Ru/TiO ₂ (5.7 wt%, 2.4 nm)	1000 mg	4:1	1	180	864 mL h ⁻¹ g _{cat} ⁻¹	100	100	0.0024	³⁷ Energy Environ. Sci. 2009

3.3. Characterization of used sample $\text{Ru}_x\text{Ti}_y\text{O}_z$

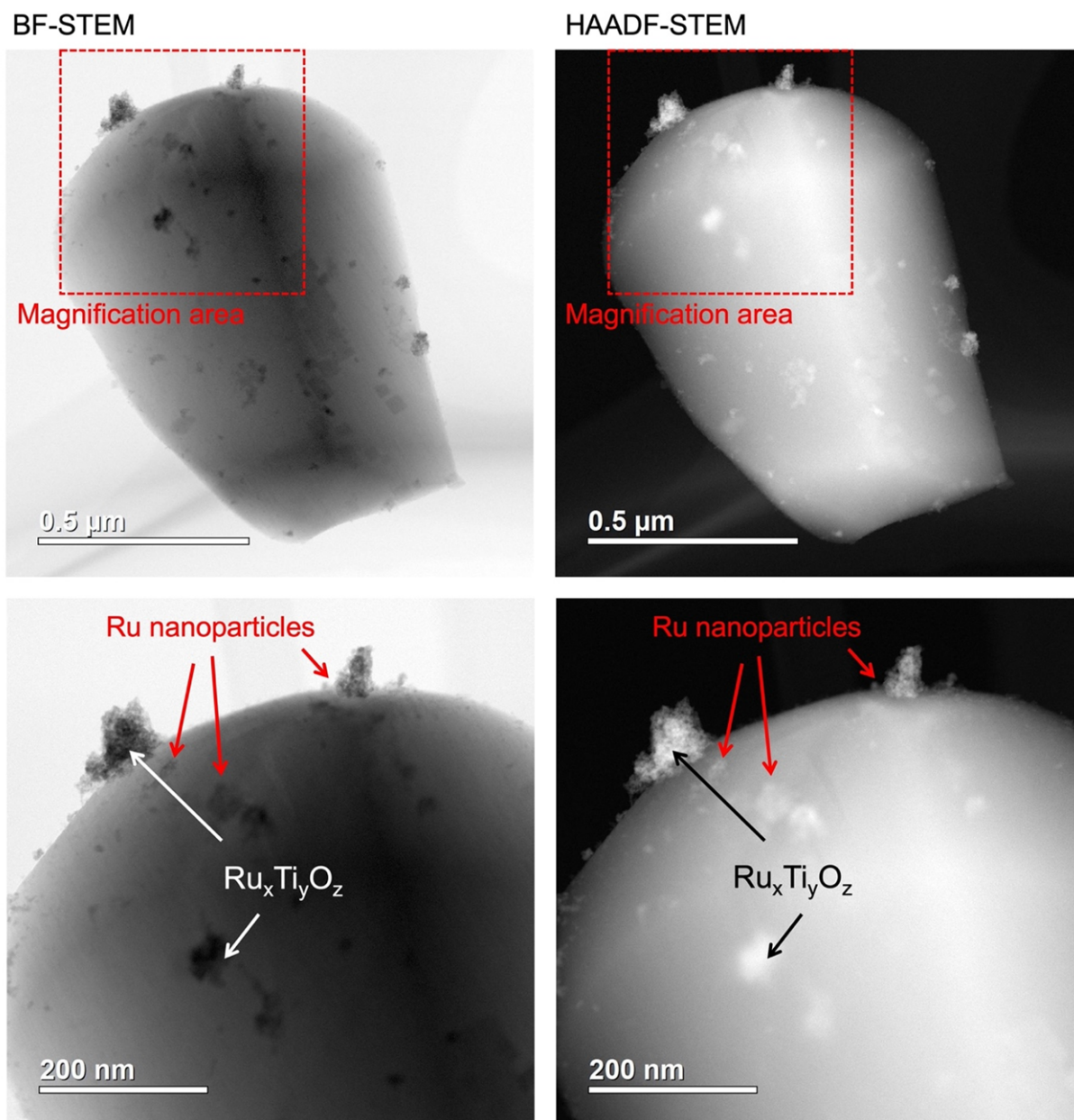


Figure S26. Low magnificant BF and HAADF-STEM image of used $\text{Ru}_x\text{Ti}_y\text{O}_z$ at 140 °C for 2h. The morphology used sample was similar with the fresh sample except the nanoporous RuO_2 reduced to Ru nanoparticles.

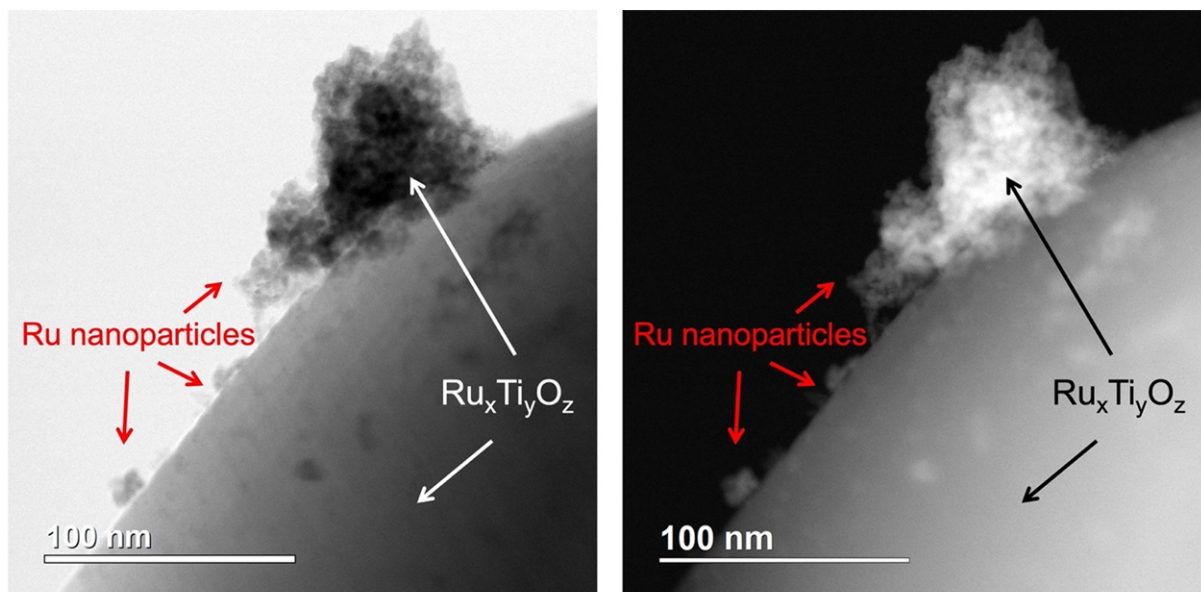


Figure S27. Low magnification BF and HAADF-STEM image of used $\text{Ru}_x\text{Ti}_y\text{O}_z$ at 140 °C for 2h.

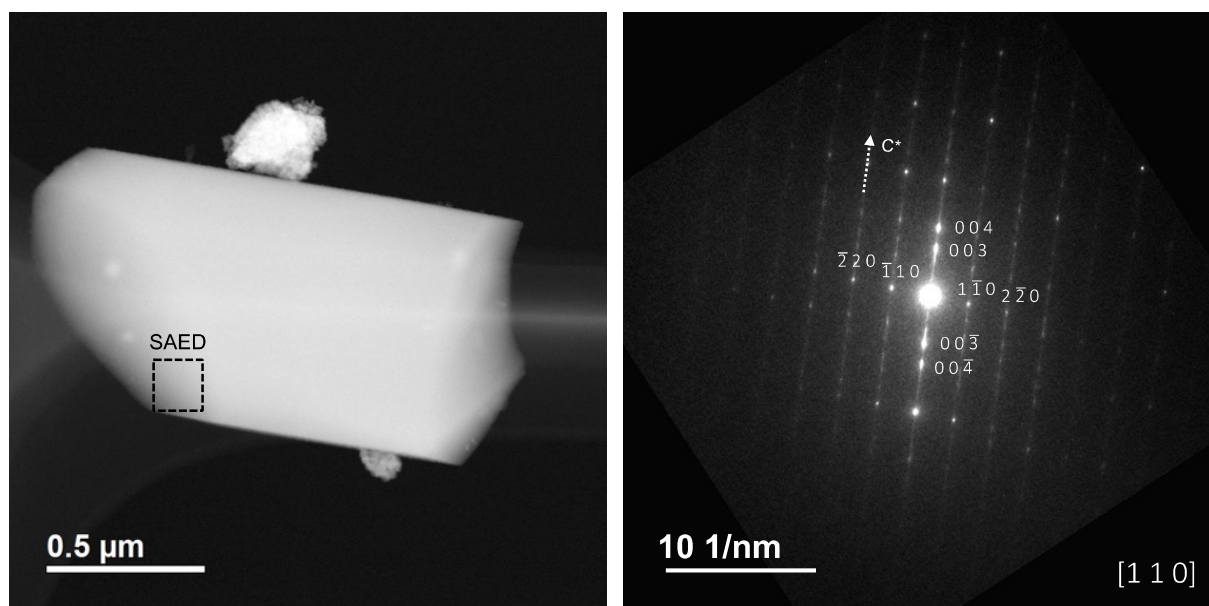


Figure S28. Low magnification HAADF-STEM image and SAED patterns along the $[110]$ zone axis of used $\text{Ru}_x\text{Ti}_y\text{O}_z$ at 140 °C for 2h. The streaking of diffraction spots on the SAED pattern of $[110]$, indicating preserve of disordered layer structure.

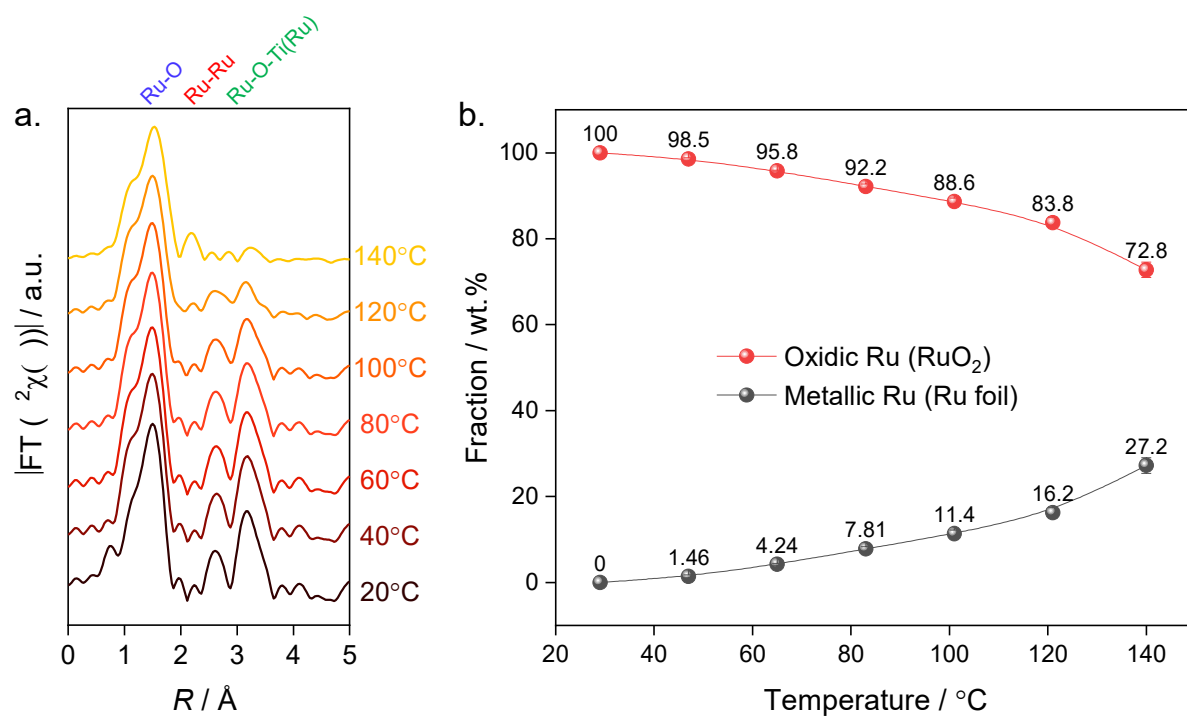


Figure S29. a, *In-situ* FT-EXAFS spectra under the ramping of the reaction temperature from 20 to 140 °C at the Ru K-edge. b, Proportion of metallic Ru and oxidic Ru from the linear combination fitting of the XANES results using Ru foil and RuO_2 as references. Initial diminish of second shell peaks with increasing amount of metallic Ru suggested the rapid reduction of ordered precipitated RuO_2 .

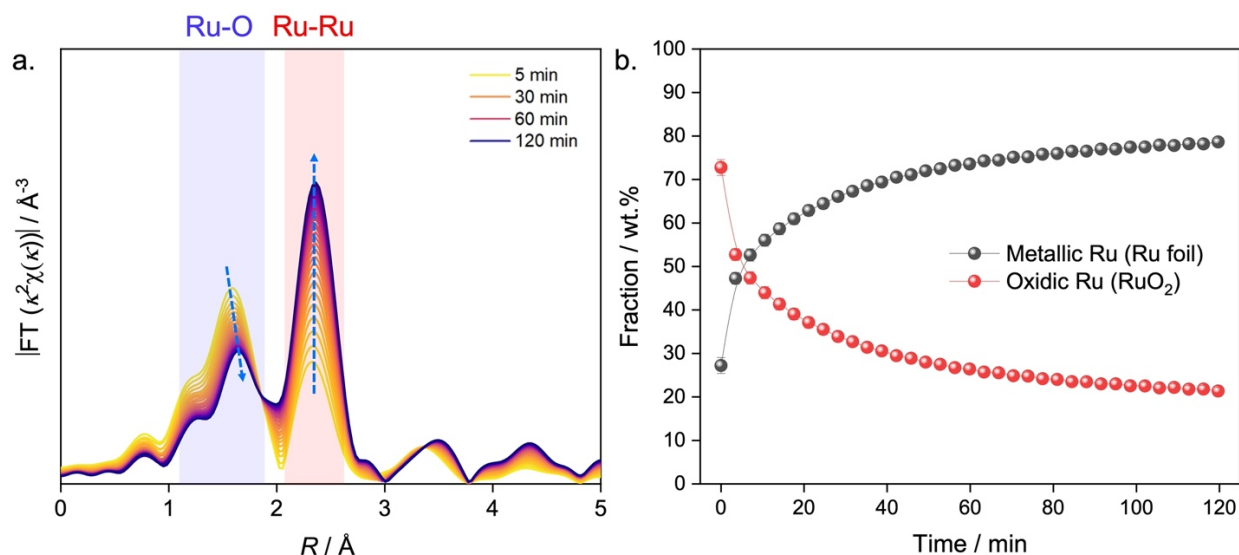


Figure S30. a, *In-situ* FT-EXAFS spectra under the reaction condition at 140 °C for 2 h at the Ru K-edge. b, Proportion of metallic Ru and oxidic Ru from the linear combination fitting of the XANES results using Ru foil and RuO₂ as references. During the first 60 min of exposure at 140 °C, oxidic Ru species reduced to metallic Ru with a steep gradient from 72.8 wt% to 25.7 wt% and stabilized around ~21 wt%. Furthermore, the expansion of the r-space to 1.657 $\text{\AA}$, accompanied by a decrease in the coordination number, demonstrated the change in the local geometric structure and valence state^{38,39}.

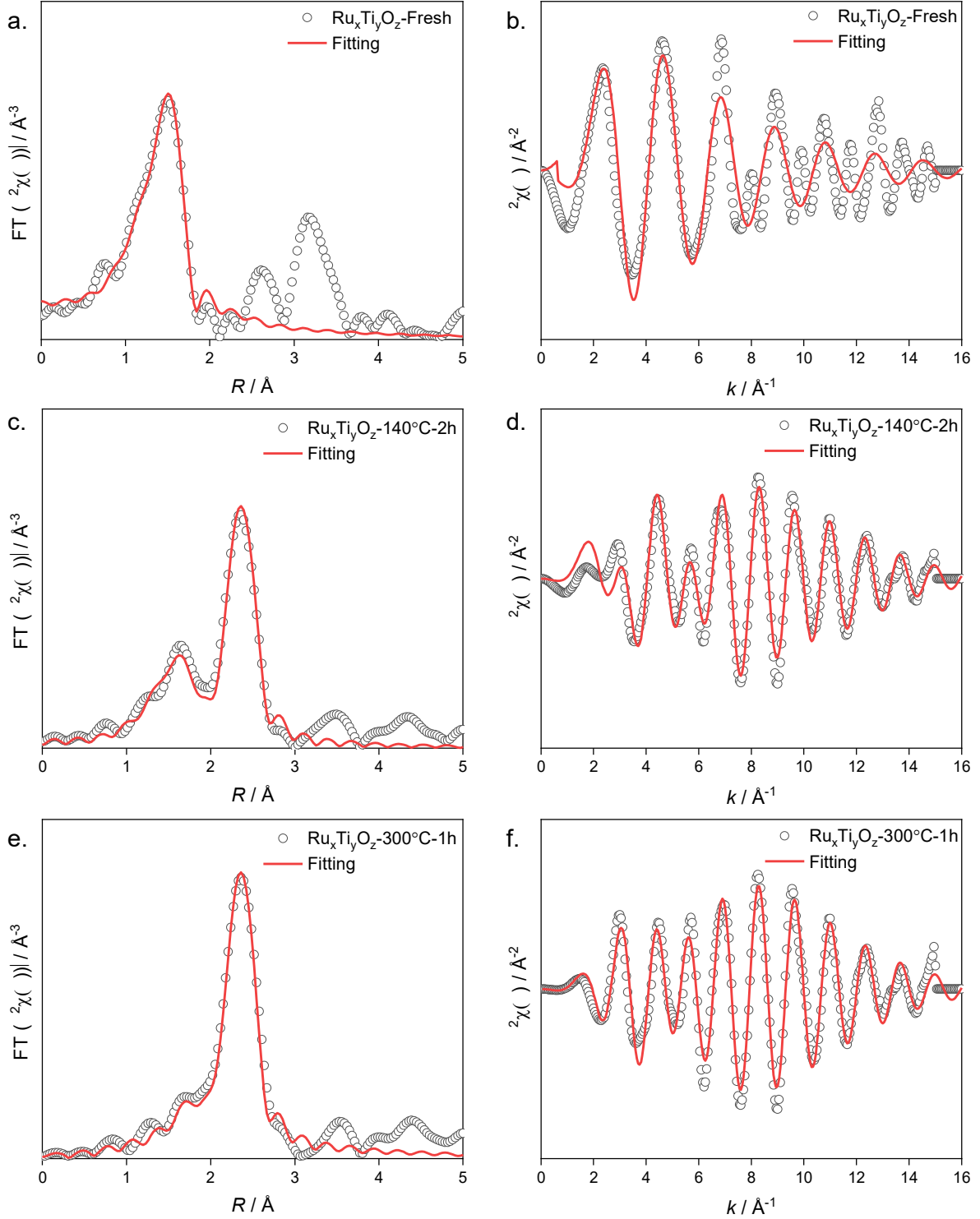


Figure S31. Fitting of k^2 -weighted *in-situ* EXAFS data of (a,b) $\text{Ru}_x\text{Ti}_y\text{O}_z$. (c,d) $\text{Ru}_x\text{Ti}_y\text{O}_z$ -140°C-2h (f) and (e,f) $\text{Ru}_x\text{Ti}_y\text{O}_z$ -300°C-1h (g) in the region of 1.0–3.0 Å. $\text{Ru}_x\text{Ti}_y\text{O}_z$ was only fitted to the first shell due to overlapping not only multiply scattering path from disordered Ru-O-Ti but Ru-O-Ru path precipitated RuO_2 on the second shell scattering.

Table S7. Summary of EXAFS fitting results of $\text{Ru}_x\text{Ti}_y\text{O}_z$. (c,d) $\text{Ru}_x\text{Ti}_y\text{O}_z$ -140°C-2h (f) and (e,f) $\text{Ru}_x\text{Ti}_y\text{O}_z$ -300°C-1h catalysts with Ru foil and RuO_2 as reference samples.

Sample	Shell	r / Å	n / atom	ΔE_0 / eV	σ^2 / *10 ⁻³ Å ²	R _{Factor}
Ru foil	Ru-Ru	2.67	12	-4.32 ± 0.80	4.47 ± 0.18	0.013
	Ru-O	1.96	6		2.62 ± 0.50	
RuO_2	Ru-Ru	3.12	2	-4.39 ± 1.56	2.62 ± 0.57	0.018
	Ru-Ru	3.55	8		2.71 ± 0.24	
$\text{Ru}_x\text{Ti}_y\text{O}_z$ -Fresh	Ru-O	1.98 ± 0.01	5.75 ± 0.52	1.46 ± 1.36	3.85 ± 0.94	0.006
$\text{Ru}_x\text{Ti}_y\text{O}_z$ -140°C-2h	Ru-O	2.03 ± 0.04	2.46 ± 0.88	-3.50 ± 1.09	7.69 ± 0.45	0.015
	Ru-Ru	2.67 ± 0.02	6.18 ± 0.75		6.72 ± 0.70	
$\text{Ru}_x\text{Ti}_y\text{O}_z$ -300°C-1h	Ru-Ru	2.66 ± 0.02	7.92 ± 0.73	-4.89 ± 0.71	7.13 ± 0.61	0.021

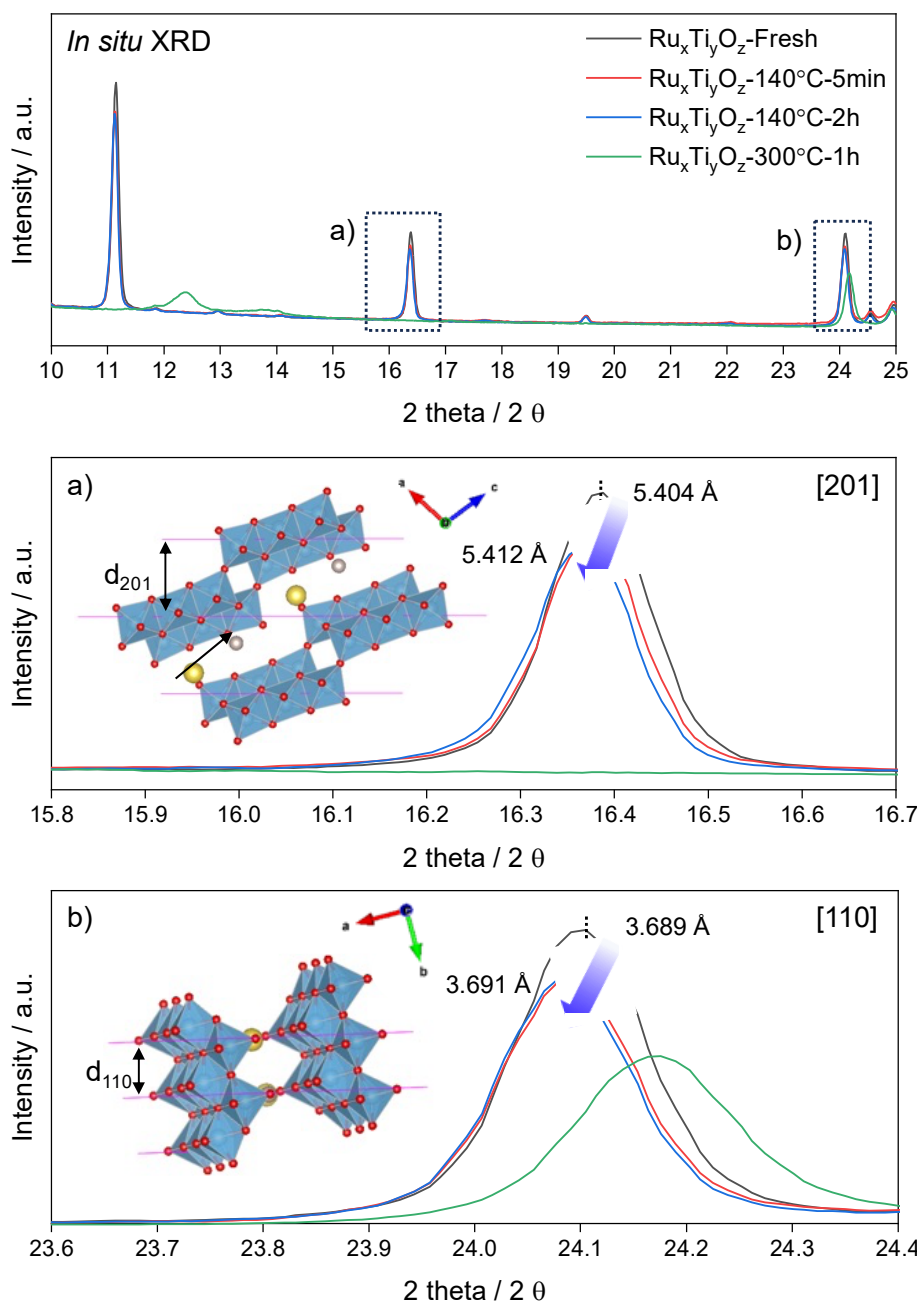


Figure S32. *In-situ* XRD spectra of $\text{Ru}_x\text{Ti}_y\text{O}_z$ collected under the difference time and reaction temperature. a) [201] plane and b) [110] plane region. [201] and [110] planes also showed the shift to the low angle in the reaction condition. The [201] plane along the c^* -axis (interlayer direction) expanded by 0.008 Å, while the [110] plane along the b^* -axis expanded by only 0.002 Å, indicating expansion along the interlayer direction. After exposure to 300 °C, the layer structure shrank significantly and differed from the fresh $\text{Ru}_x\text{Ti}_y\text{O}_z$ structure. Atomic structures were visualized using VESTA⁴⁰.

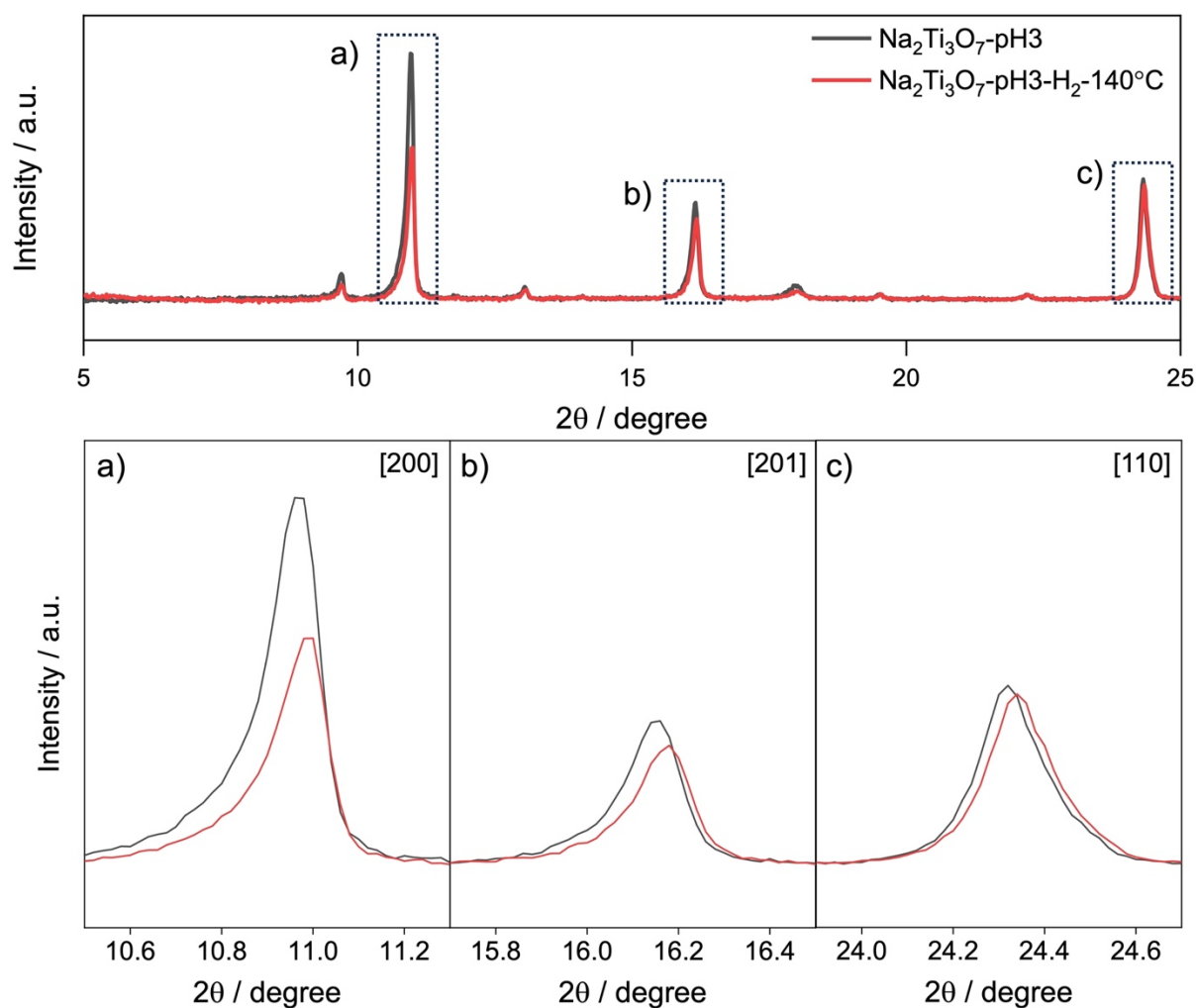


Figure S33. X-ray diffraction (XRD) spectra of $\text{Na}_2\text{Ti}_3\text{O}_7\text{-pH3}$ and $\text{Na}_2\text{Ti}_3\text{O}_7\text{-pH3-H}_2\text{-140}^\circ\text{C}$. a) [200] plane, b) [201] plane, and c) [110] plane region. General $\text{Na}_2\text{Ti}_3\text{O}_7$ like structure shrink its layered distance along increase in exposure temperature by dehydration and slip of interlayer structure⁴¹.

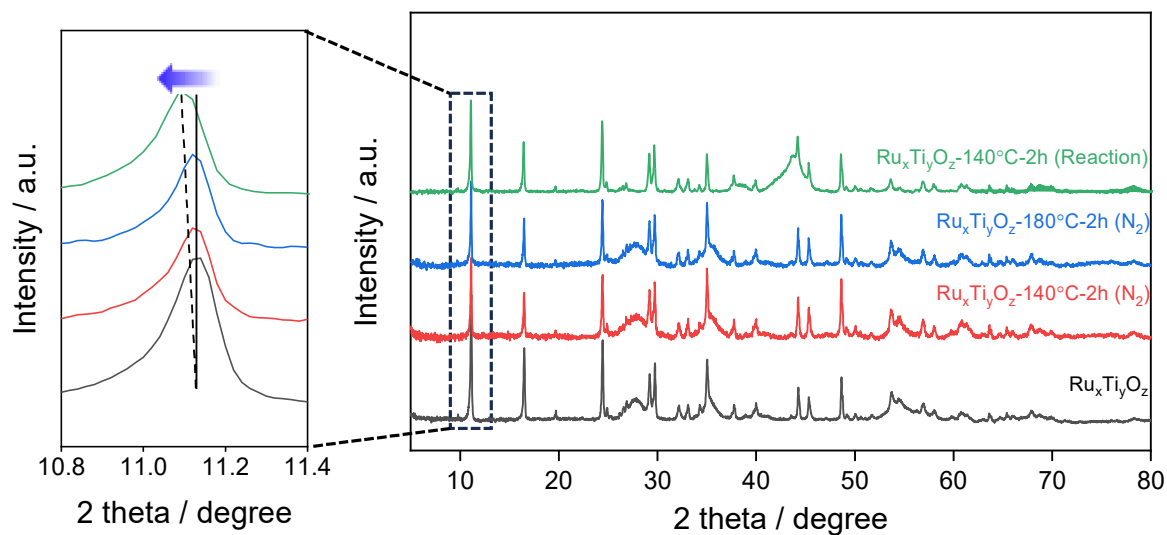


Figure S34. X-ray diffraction (XRD) spectra comparison between $\text{Ru}_x\text{Ti}_y\text{O}_z$ after reaction at 140 °C and after N_2 treatment at 140 and 180 °C, respectively. In contrast to $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Ru}_x\text{Ti}_y\text{O}_z$ treated in N_2 condition, the exposure of $\text{Ru}_x\text{Ti}_y\text{O}_z$ in reducible condition increased the interlayer distance, indicating the partial reduction of Ru^{4+} to low valent Ru^{n+} ($1 \leq n \leq 3$) and maintaining its structure even exposure in air condition.

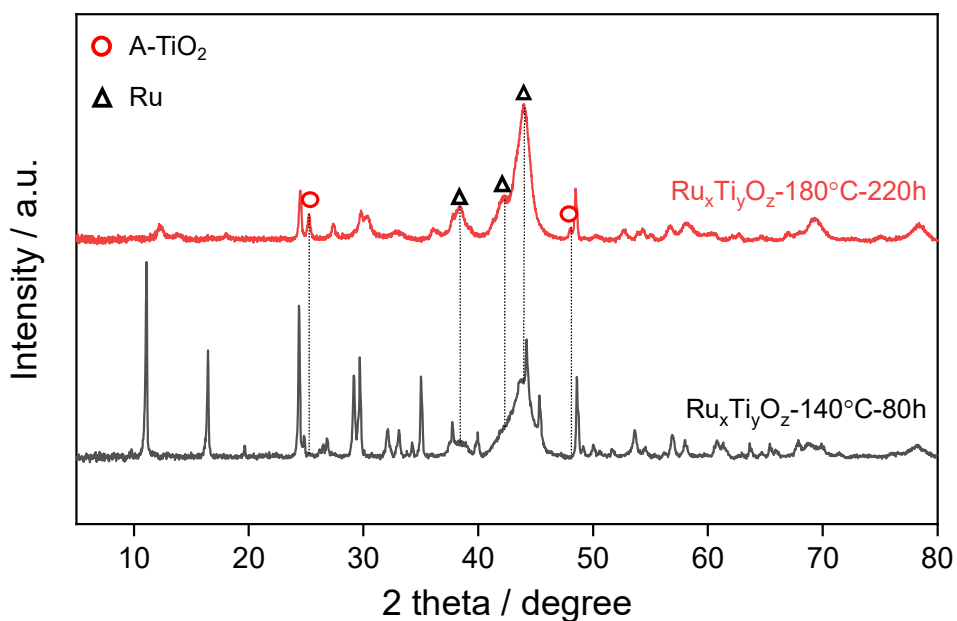


Figure S35. X-ray diffraction (XRD) spectra of used Ru_xTi_yO_z samples after long term stability test at 140 and 180 °C. Even after 80 h of long-term stability test at 140 °C, the Ru_xTi_yO_z maintained its layered structure. With respect to 180 °C-220 h, the layered structure was preserved, but an obvious decrease in intensity accompanied with the appearance of A-TiO₂ implied the loss of layered structure with long-term use, thereby deactivating the catalyst.

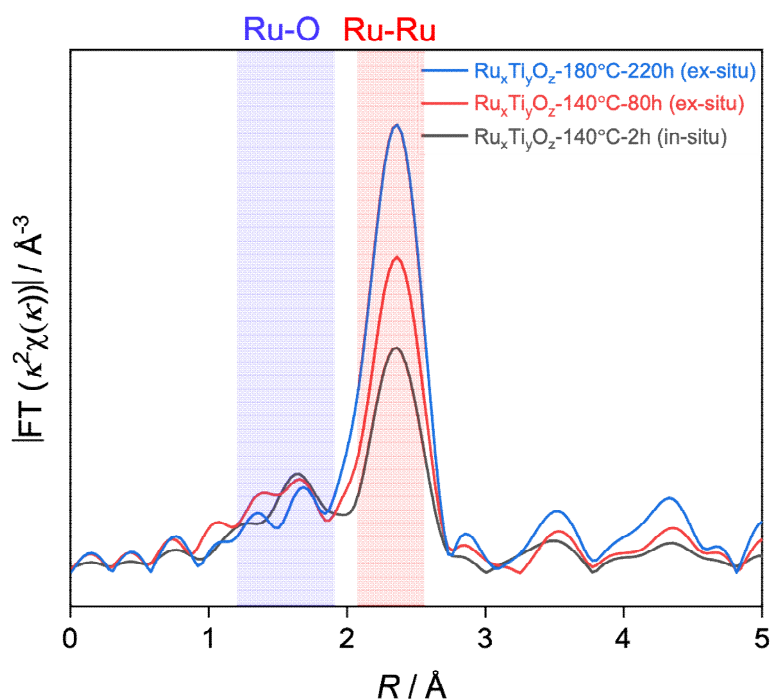


Figure. S36. FT-EXAFS spectra of used Ru_xTi_yO_z samples after long-term stability test at 140 and 180 °C at the Ru K-edge. The oxidic Ru was well preserved after long-term use of the catalyst. Nevertheless, a significant enhancement of the Ru-Ru peak was observed. This was attributed to both the aggregation of reduced metallic Ru, mainly driven by precipitated RuO₂, and the continuous reduction of ionic Ru by the gradual decay of the layered structure.

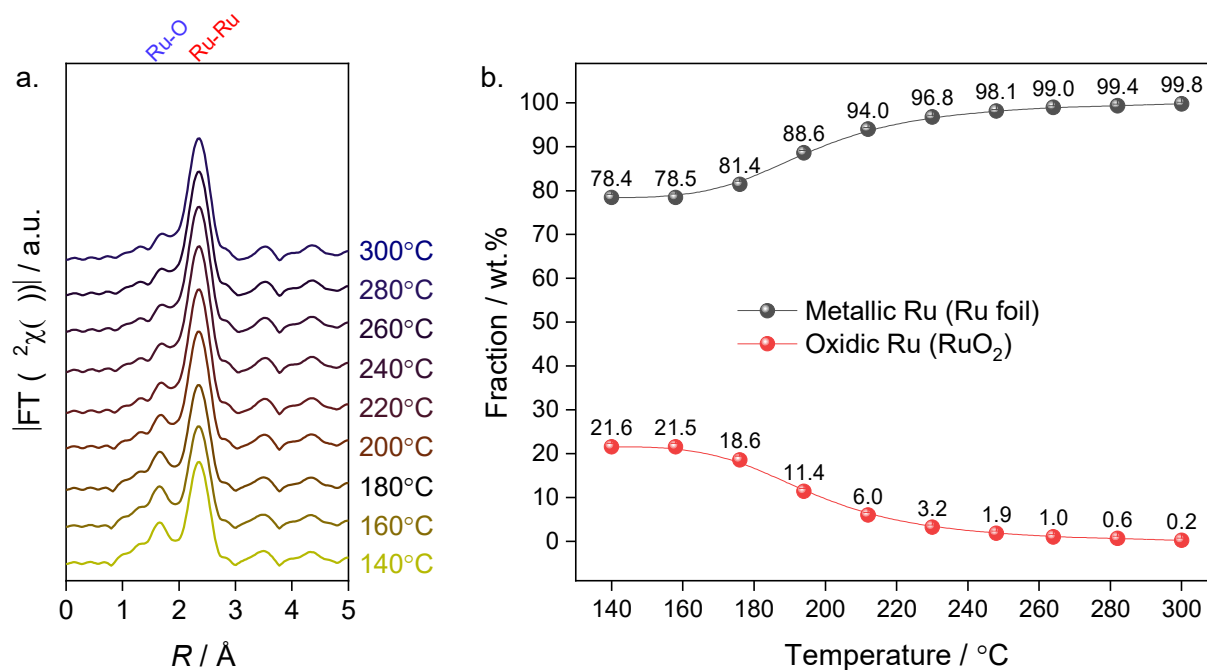


Figure S37. a, *In-situ* FT-EXAFS spectra under the ramping the reaction temperature from 140 to 300 °C at the Ru K-edge. b, Proportion of metallic Ru and oxidic Ru from the linear combination fitting of the XANES results using Ru foil and RuO₂ as references. There was clear decrease of oxidic Ru species from 180 °C, reaching near ~100 % reduction to metallic Ru. The decrease of oxidic Ru species around 180 °C was surprising well matched with the starting point of distortion of layered structure, suggesting the ionic Ru reduced to metallic Ru.

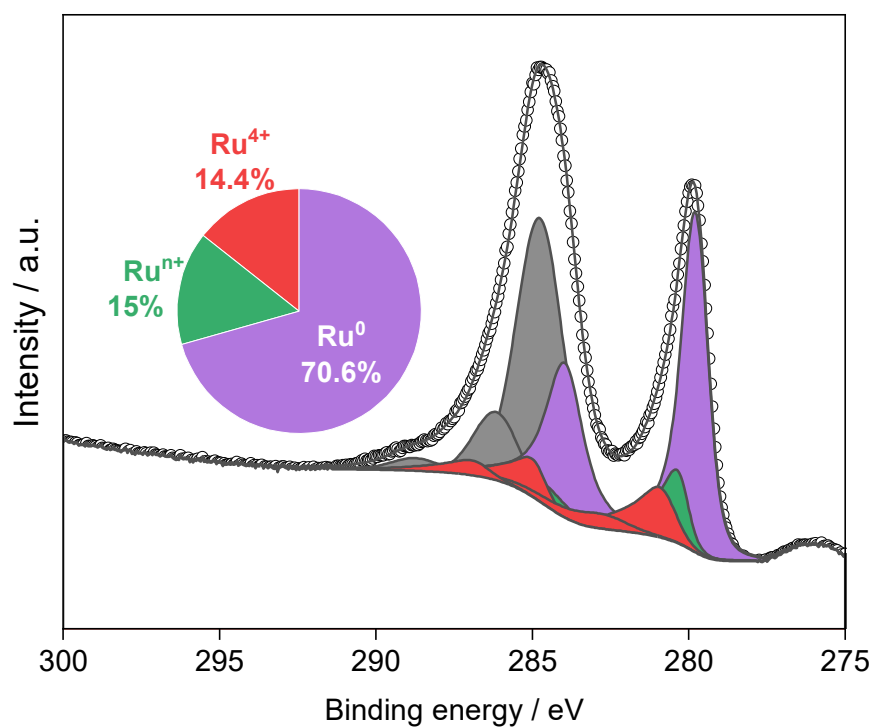


Figure S38. Ru 3d XPS spectra of used $\text{Ru}_x\text{Ti}_y\text{O}_z$ sample after reaction at 180 °C for 24h.

Table S8. Atomic fraction (at.%) of the different ruthenium species from XPS.

	Ru^0	Ru^{n+}	Ru^{4+}
$\text{Ru}_x\text{Ti}_y\text{O}_z$	0	0	100
$\text{Ru}_x\text{Ti}_y\text{O}_z$ -140°C-24h	35.8	46.4	17.8
$\text{Ru}_x\text{Ti}_y\text{O}_z$ -180°C-24h	70.6	15	14.4
$\text{Ru}_x\text{Ti}_y\text{O}_z$ -300°C-24h	91.7	3.3	4.9

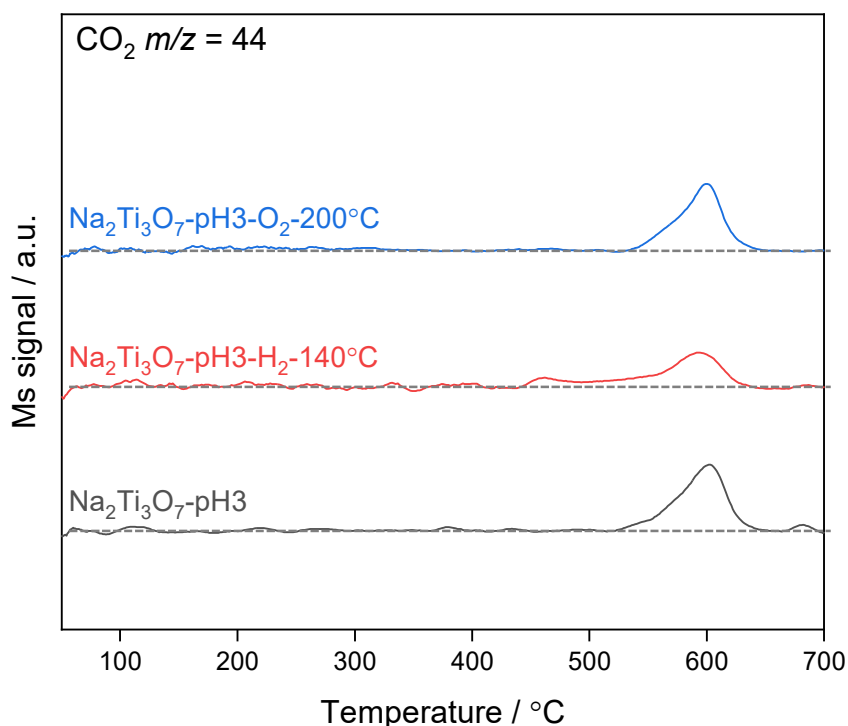


Figure. S39. CO₂-TPD spectra of Na₂Ti₃O₇-pH₃ after H₂ and O₂ pretreatments. There were no active sites for CO₂ adsorption on fresh and reduced Na₂Ti₃O₇-pH₃. In addition, oxidation of Na₂Ti₃O₇-pH₃ was carried out to confirm the function of (Ti₃O₇)²⁻ since the intercalated H⁺ was deprotonated to H₂O, and the (Ti₃O₇)²⁻-layer with unequal charge distribution might remain, which could act as a Lewis active site. However, Na₂Ti₃O₇-pH₃-O₂-200 °C also showed no obvious desorption peak, indicating that all active sites for CO₂ adsorption were associated with low-valence Ru species. The desorption peak at 600 °C in all CO₂-TPD measurements using Na₂Ti₃O₇ as a precursor may correspond to the decomposition of residual Na₂CO₃ or interstitial carbon in Na₂Ti₃O₇, where a similar peak was identified in H₂-TPR⁴².

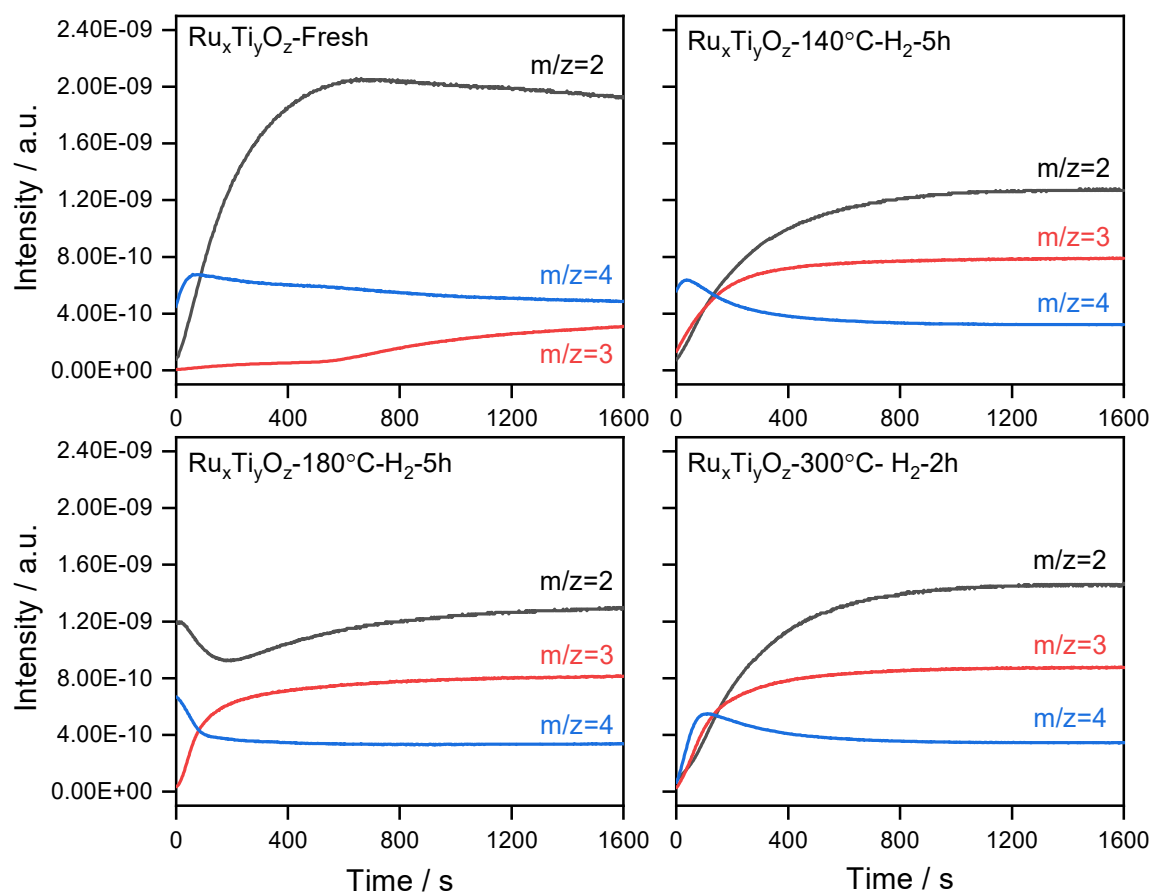


Figure. S40. H_2 - D_2 exchange experiments of $\text{Ru}_x\text{Ti}_y\text{O}_z$ at 25 °C after different reduction temperatures.

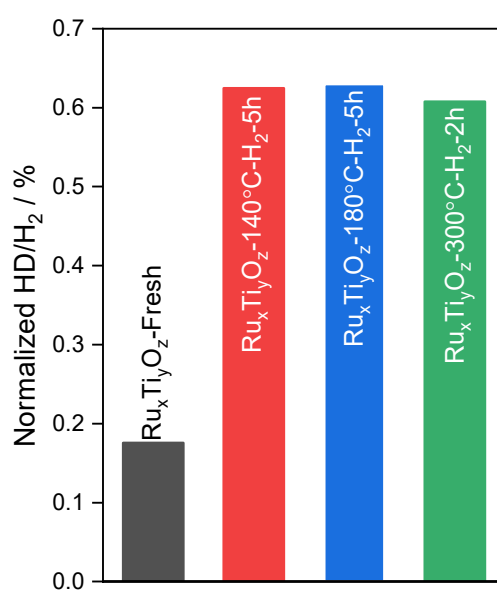


Figure S41. HD formation normalized to H_2 at 25 °C (HD/ H_2).

4. Scalability of $\text{Ru}_x\text{Ti}_y\text{O}_z$

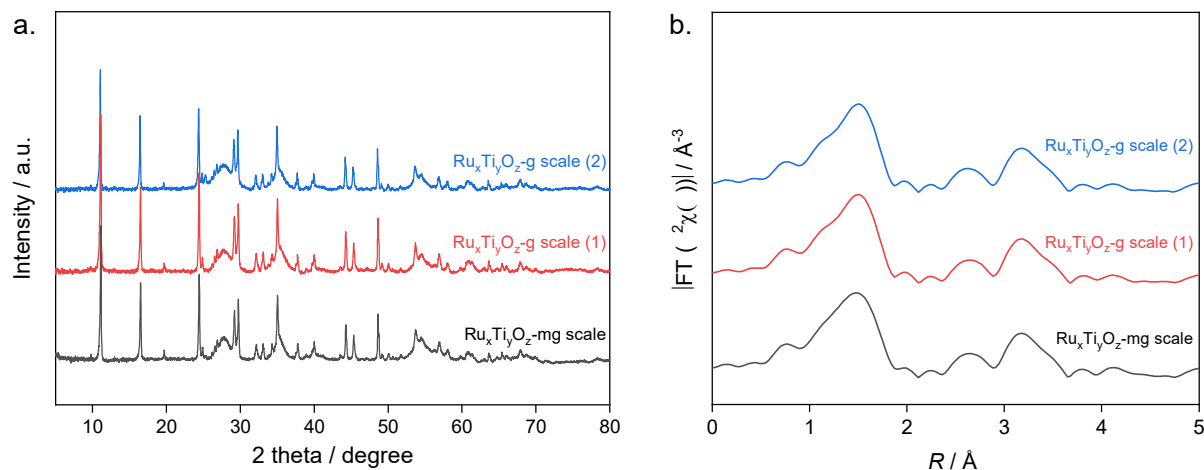


Figure. S42. a, XRD spectra and b, Ru K-edge FT-EXAFS spectra of $\text{Ru}_x\text{Ti}_y\text{O}_z$ prepared in mg and g scale.

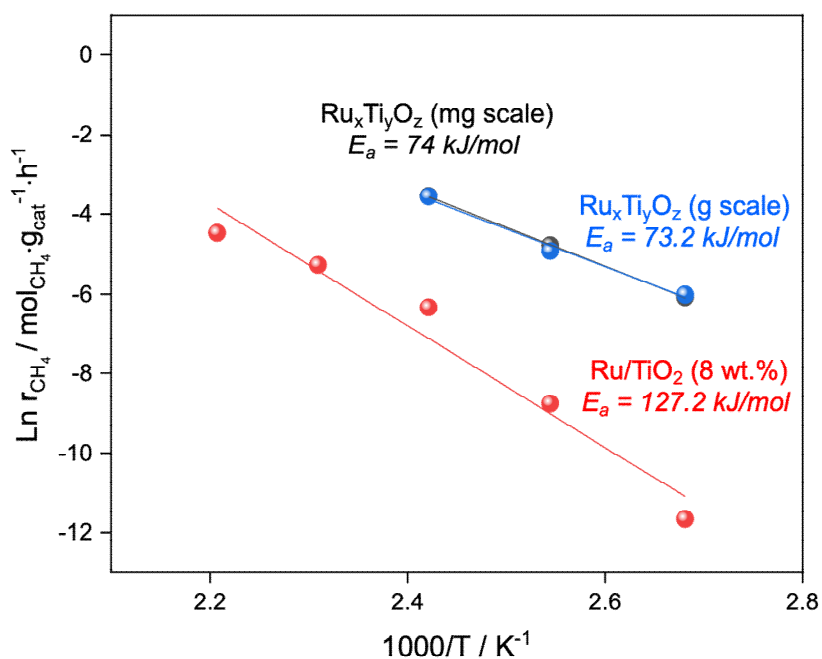


Figure. S43. Arrhenius plots obtained from CO_2 methanation on Fig. 6e with calculated apparent activation energies. There was significant difference on the activation energy between $\text{Ru}_x\text{Ti}_y\text{O}_z$ and Ru/TiO_2 , implying the active site of $\text{Ru}_x\text{Ti}_y\text{O}_z$ was nonidentical as conventional supported Ru/TiO_2 .

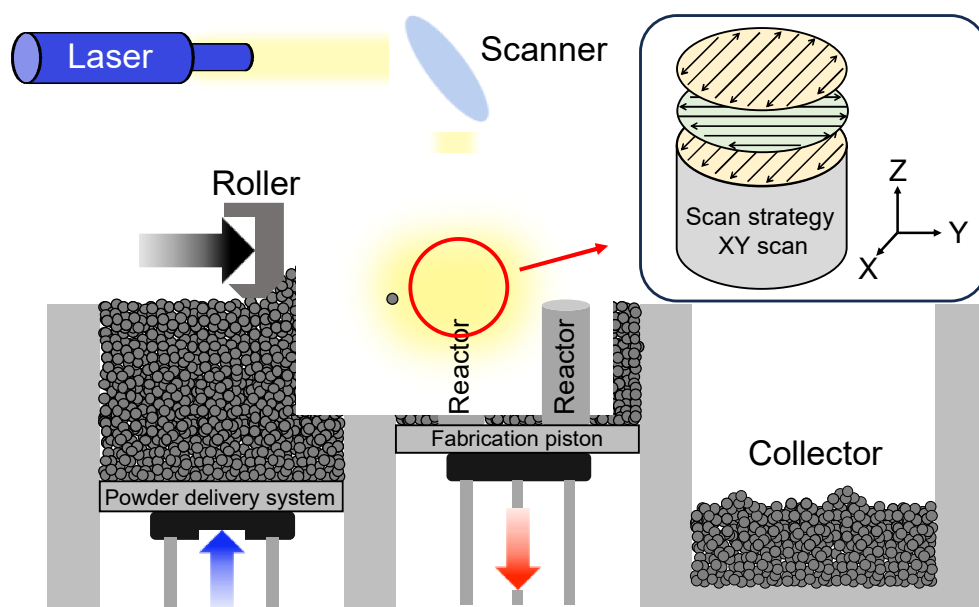


Figure. S44. Schematic illustration of selective laser melting (SLM) process with XY scan strategy.

Table S9. Ti alloy powder components. (Average particle size: 49.7 μm)

Element	Ti	Al	V	O	N	H	Fe	C	Y
wt.%	Bal	6.35	4.15	0.077	0.006	0.002	0.2	0.01	<0.005

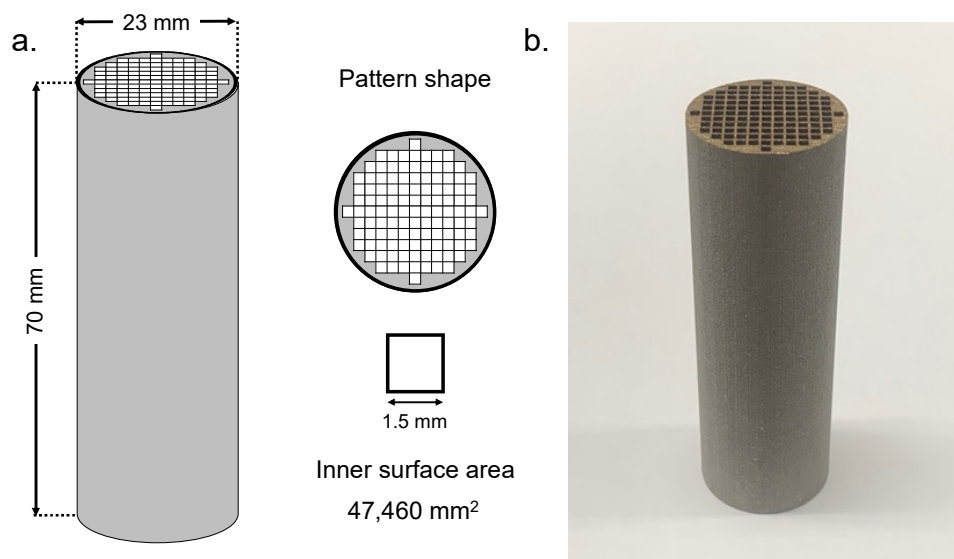


Figure. S45. a, Schematic illustration of pattern of Ti-SCR. b, Photograph of Ti-SCR.

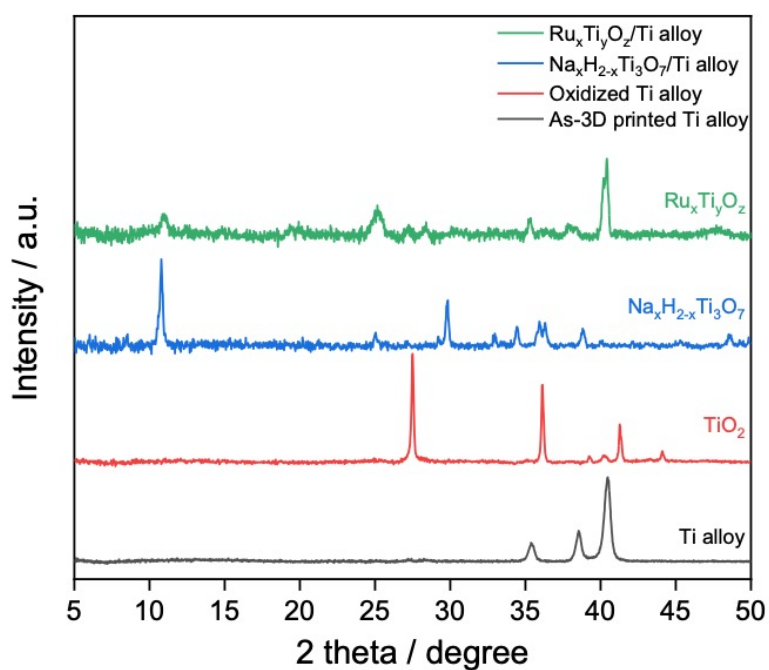


Figure. S46. XRD spectra of as-printed, oxidized, as-synthesized Na_xH_{2-x}Ti₃O₇, and Ru_xTi_yO_z on the 3D Ti self-catalytic reactor (SCR).

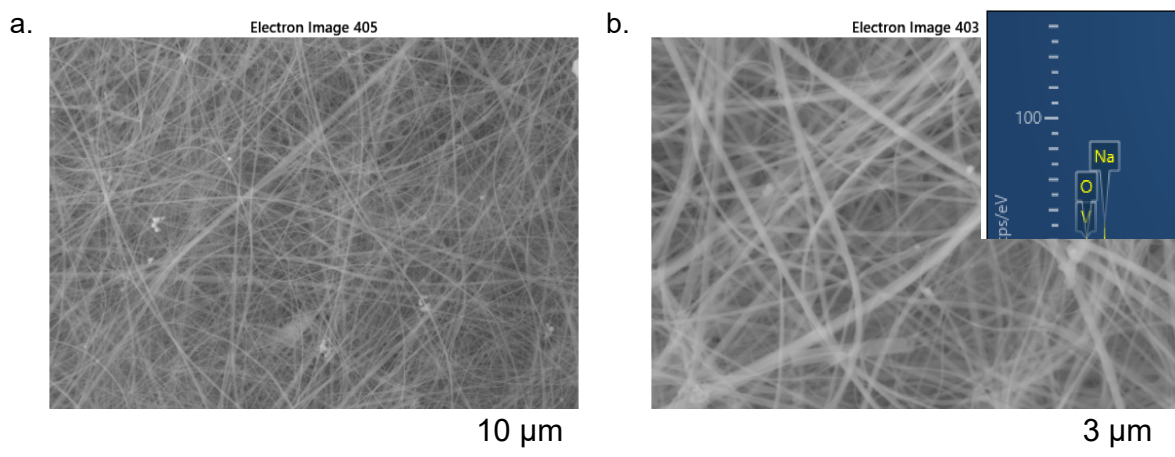


Figure. S47. Morphology and composition of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7/\text{Ti}$ SCR measured by SEM/EDS. $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ was successfully synthesized over the Ti SCR through the oxidation-hydrothermal process⁴³.

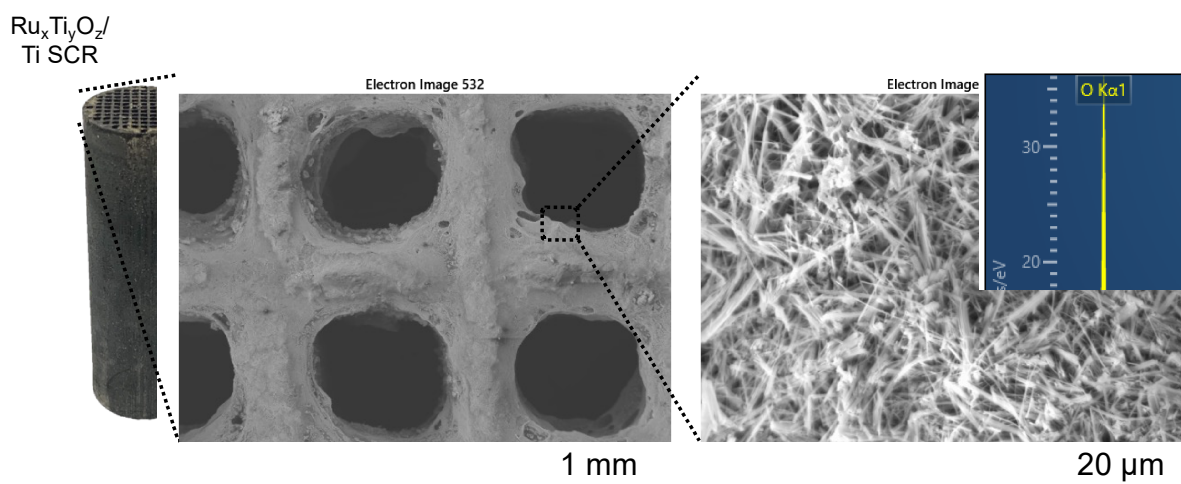


Figure. S48. Morphology and composition of $\text{Ru}_x\text{Ti}_y\text{O}_z/\text{Ti}$ SCR measured by SEM/EDS.

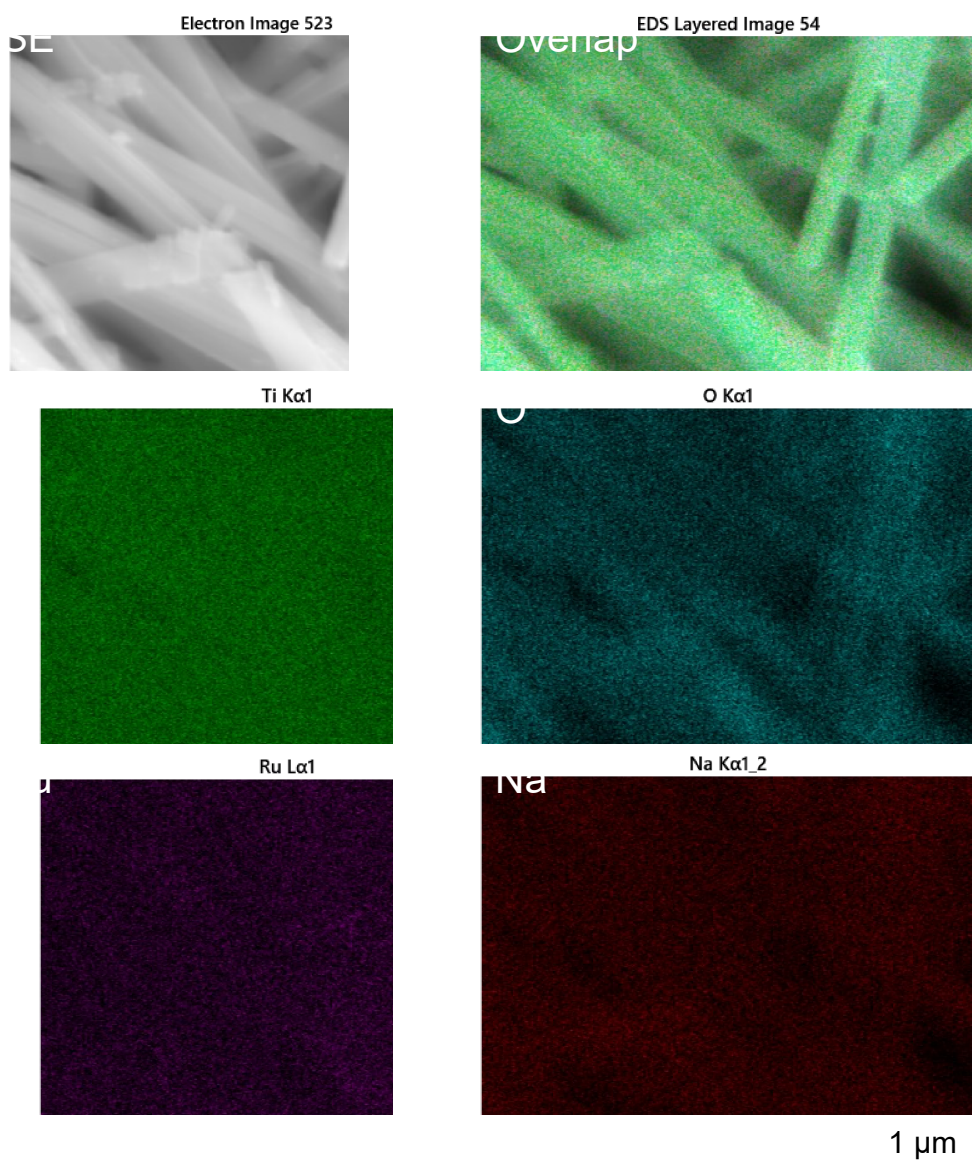


Figure S49. SEM/EDS mapping results of $\text{Ru}_x\text{Ti}_y\text{O}_z/\text{Ti}$ SCR with high magnification.

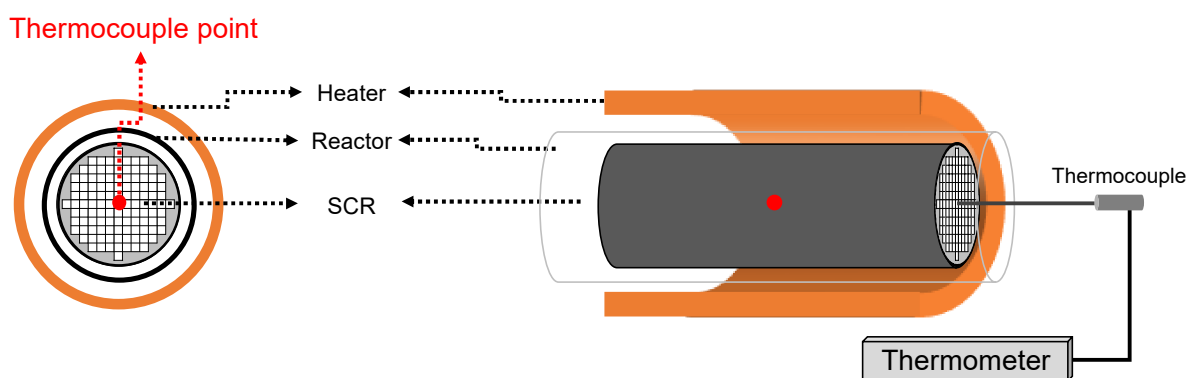


Figure S50. Schematic diagram of the thermocouple position for Ti SCR.

5. Supplementary References

1. Kim, A. *et al.* Selective CO₂ methanation on Ru/TiO₂ catalysts: Unravelling the decisive role of the TiO₂ support crystal structure. *Catal Sci Technol* **6**, 8117–8128 (2016).
2. Tébar-Soler, C. *et al.* Low-oxidation-state Ru sites stabilized in carbon-doped RuO₂ with low-temperature CO₂ activation to yield methane. *Nat Mater* (2023) doi:10.1038/s41563-023-01540-1.
3. Morgan, D. J. Resolving ruthenium: XPS studies of common ruthenium materials. *Surface and Interface Analysis* **47**, 1072–1079 (2015).
4. Bi, J. *et al.* Titanate for water remediation: Synthesis, application, mechanism and optimization. *J Mater Chem A Mater* **8**, 14415–14440 (2020).
5. Kondo, Y., Goto, T. & Sekino, T. Sr²⁺sorption property of seaweed-like sodium titanate mats: Effects of crystallographic properties. *RSC Adv* **11**, 18676–18684 (2021).
6. Li, N. *et al.* Highly efficient, irreversible and selective ion exchange property of layered titanate nanostructures. *Adv Funct Mater* **22**, 835–841 (2012).
7. Luxton, T. P., Eick, M. J. & Scheckel, K. G. Characterization and dissolution properties of ruthenium oxides. *J Colloid Interface Sci* **359**, 30–39 (2011).
8. Musi, S., Popovi, S., Maljkovi, M., Furi, K. & Gajovi, A. Influence of synthesis procedure on the formation of RuO₂. *Mater Lett* **56**, 806–811 (2002).
9. Wang, Y., Xiao, R., Hu, Y. S., Avdeev, M. & Chen, L. P2-Na_{0.6} [Cr_{0.6} Ti_{0.4}]O₂ cation-disordered electrode for high-rate symmetric rechargeable sodium-ion batteries. *Nat Commun* **6**, 1–9 (2015).
10. Liu, W., Zhang, P., Borthwick, A. G. L., Chen, H. & Ni, J. Adsorption mechanisms of thallium(I) and thallium(III) by titanate nanotubes: Ion-exchange and co-precipitation. *J Colloid Interface Sci* **423**, 67–75 (2014).
11. McKeown, D. A. *et al.* Structure of hydrous ruthenium oxides: Implications for charge storage. *Journal of Physical Chemistry B* **103**, 4825–4832 (1999).
12. Zhan, B. *et al.* Zeolite-Confined Nano-RuO₂: A Green, Selective, and Efficient Catalyst for Aerobic Alcohol Oxidation environmental reasons (Scheme 1). Many catalytic systems, for. *J. Am. Chem. Soc.* **125**, 2195–2199 (2003).
13. Sheng, G., Dong, H., Shen, R. & Li, Y. Microscopic insights into the temperature-dependent adsorption of Eu(III) onto titanate nanotubes studied by

- FTIR, XPS, XAFS and batch technique. *Chemical Engineering Journal* **217**, 486–494 (2013).
14. Kondo, Y., Goto, T. & Sekino, T. Sr²⁺sorption property of seaweed-like sodium titanate mats: Effects of crystallographic properties. *RSC Adv* **11**, 18676–18684 (2021).
 15. Cao, Y. *et al.* A New Triclinic Phase Na₂Ti₃O₇ Anode for Sodium-Ion Battery. *Adv Funct Mater* **30**, (2020).
 16. Koningsberger, D. C., Mojet, B. L., Van Dorssen, G. E. & Ramaker, D. E. XAFS spectroscopy; fundamental principles and data analysis. *Top Catal* **10**, 143–155 (2000).
 17. Farges, F. & Brown, G. E. Ti-edge XANES studies of Ti coordination and disorder in oxide compounds: Comparison between theory and experiment. *Phys Rev B Condens Matter Mater Phys* **56**, 1809–1819 (1997).
 18. Matsuo, S., Sakaguchi, N. & Wakita, H. Pre-edge features of Ti K-edge X-ray absorption near-edge structure for the local structure of sol-gel titanium oxides. *Analytical Sciences* **21**, 805–809 (2005).
 19. Akimoto, J. *et al.* Soft-Chemical Synthesis and Electrochemical Property of H₂Ti₁₂O₂₅ as a Negative Electrode Material for Rechargeable Lithium-Ion Batteries. *J Electrochem Soc* **158**, A546 (2011).
 20. Hengne, A. M., Biradar, N. S. & Rode, C. V. Surface species of supported ruthenium catalysts in selective hydrogenation of levulinic esters for bio-refinery application. *Catal Letters* **142**, 779–787 (2012).
 21. Mori, K., Miyawaki, K. & Yamashita, H. Ru and Ru-Ni Nanoparticles on TiO₂ Support as Extremely Active Catalysts for Hydrogen Production from Ammonia-Borane. *ACS Catal* **6**, 3128–3135 (2016).
 22. Tébar-Soler, C. *et al.* Low-oxidation-state Ru sites stabilized in carbon-doped RuO₂ with low-temperature CO₂ activation to yield methane. *Nat Mater* **22**, (2023).
 23. Tang, Y. *et al.* Ruthenium-Cobalt Solid-Solution Alloy Nanoparticles for Enhanced Photopromoted Thermocatalytic CO₂ Hydrogenation to Methane. *ACS Nano* **18**, 11449–11461 (2024).
 24. Nyman, M. & Hobbs, D. T. A family of peroxo-titanate materials tailored for optimal strontium and actinide sorption. *Chemistry of Materials* **18**, 6425–6435 (2006).

25. Zhou, J. *et al.* Interfacial compatibility critically controls Ru/TiO₂ metal-support interaction modes in CO₂ hydrogenation. *Nat Commun* **13**, 1–10 (2022).
26. Tang, X. *et al.* Thermally stable Ni foam-supported inverse CeAlO_x/Ni ensemble as an active structured catalyst for CO₂ hydrogenation to methane. *Nat Commun* **15**, (2024).
27. Xu, X. *et al.* Facile Cr³⁺-doping strategy dramatically promoting Ru/CeO₂ for low-temperature CO₂ methanation: Unraveling the roles of surface oxygen vacancies and hydroxyl groups. *ACS Catal* **11**, 5762–5775 (2021).
28. Zhang, T. *et al.* The dual-active-site tandem catalyst containing Ru single atoms and Ni nanoparticles boosts CO₂ methanation. *Appl Catal B* **323**, 122190 (2023).
29. Cisneros, S. *et al.* Oxygen vacancies in Ru/TiO₂ - drivers of low-temperature CO₂ methanation assessed by multimodal operando spectroscopy. *iScience* **25**, (2022).
30. Xin, H. *et al.* Overturning CO₂ Hydrogenation Selectivity with High Activity via Reaction-Induced Strong Metal-Support Interactions. *J Am Chem Soc* **144**, 4874–4882 (2022).
31. Cored, J. *et al.* Hydrothermal Synthesis of Ruthenium Nanoparticles with a Metallic Core and a Ruthenium Carbide Shell for Low-temperature Activation of CO₂ to Methane. *J Am Chem Soc* **141**, 19304–19311 (2019).
32. Dreyer, J. A. H. *et al.* Influence of the oxide support reducibility on the CO₂ methanation over Ru-based catalysts. *Appl Catal B* **219**, 715–726 (2017).
33. Quindimil, A. *et al.* Effect of metal loading on the CO₂ methanation: A comparison between alumina supported Ni and Ru catalysts. *Catal Today* **356**, 419–432 (2020).
34. Chen, S. *et al.* Raising the CO_x Methanation Activity of a Ru/γ-Al₂O₃ Catalyst by Activated Modification of Metal–Support Interactions. *Angewandte Chemie - International Edition* **59**, 22763–22770 (2020).
35. Petala, A. & Panagiotopoulou, P. Methanation of CO₂ over alkali-promoted Ru/TiO₂ catalysts: I. Effect of alkali additives on catalytic activity and selectivity. *Appl Catal B* **224**, 919–927 (2018).
36. Lin, Q. *et al.* Crystal phase effects on the structure and performance of ruthenium nanoparticles for CO₂ hydrogenation. *Catal Sci Technol* **4**, 2058–2063 (2014).

37. Abe, T., Tanizawa, M., Watanabe, K. & Taguchi, A. CO₂ methanation property of Ru nanoparticle-loaded TiO₂ prepared by a polygonal barrel-sputtering method. *Energy Environ Sci* **2**, 315–321 (2009).
38. Donakowski, M. D. *et al.* Trapping a Ru₂O₃ Corundum-like Structure at Ultrathin, Disordered RuO₂ Nanoskins Expressed in 3D. *Journal of Physical Chemistry C* **122**, 28895–28900 (2018).
39. Liu, D. *et al.* In situ constructing atomic interface in ruthenium-based amorphous hybrid-structure towards solar hydrogen evolution. *Nat Commun* **14**, (2023).
40. Momma, K. & Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Applied Crystallography* **44**, 1272–1276 (2011).
41. Morgado, E. *et al.* A study on the structure and thermal stability of titanate nanotubes as a function of sodium content. *Solid State Sci* **8**, 888–900 (2006).
42. Wigmans, T., van Doorn, J. & Moulijn, J. A. Temperature-programmed desorption study of Na₂CO₃-containing activated carbon. *Fuel* **62**, 190–195 (1983).
43. Tang, H., Zhou, Z. & Sodano, H. A. Relationship between BaTiO₃ nanowire aspect ratio and the dielectric permittivity of nanocomposites. *ACS Appl Mater Interfaces* **6**, 5450–5455 (2014).