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Layered Na₂Ti₃O₇-supported Ru catalyst for ambient CO₂ methanation

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The methanation of CO_2 offers a practical solution for storing renewable energy and mitigating global climate risks. However, the primary challenge lies in achieving efficient CH_4 production at lower temperatures. Here, we report a layered $Na_2Ti_3O_7$ -supported Ru catalyst as a stabilizer of low-valence Ru that enables CO_2 activation at low temperatures. This catalyst leads to a CH_4 production rate of 33.6 and 139.1 mmol $g_{cat}^{-1} h^{-1}$ at 140 and 180 °C, respectively, with a gas hourly space velocity of 24,000 mL g⁻¹ h⁻¹ at ambient pressure (1 bar), significantly surpassing state-of-the-art catalysts performance. Moreover, the catalyst demonstrates robustness to on-off intermittency and 220hour long-term stability tests, indicating its reliability under challenging conditions. The catalyst is also successfully synthesized at the gram scale and on a 3D-printed metal self-catalytic reactor by a facile ion-exchange method, confirming its excellent scalability. This study marks a significant step forward in the design of catalysts for the low temperature CO_2 hydrogenation.

Natural gas is a representative primary energy source, of which 4037.5 billion cubic meters (25% of global energy consumption) was consumed in 2021, which is a 2.2% increase on average from 2011 to 2021¹. However, the majority of natural gas is still extracted from deep underground, which causes a continuous rise in the net CO₂ in the Earth's atmosphere, and thereby remains an obstacle to the achievement of a sustainable society². Natural gas is geographically concentrated in specific countries, which is a critical issue in terms of the global energy supply chain and national security because supply could suddenly become short due to unexpected issues³. For instance, Russia, which is responsible for 23.6% of global natural gas, invaded Ukraine, which resulted in an energy price hike to ten times higher than pre-pandemic price levels (\$16-22 MW h⁻¹ to $108-216 \text{ MW h}^{-1}$ in 2022⁴. This became an enormous energy crisis for households as well as global industries. Therefore, an essential alternative route to obtain natural gas should be proposed to resolve such issues.

Methane synthesized by the Sabatier reaction (as known as CO_2 methanation, $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, $\Delta H = -165.0$ kJ mol⁻¹) in a power-to-gas (P2G) compartment can be a promising and realistic alternative methodology to the extraction of natural gas from natural sources⁵. Green H₂ generated from renewable energy with waste CO₂ can be used to produce methane (CH₄) with net-zero emission and can be readily utilized with the well-established infrastructure that would easily facilitate long-term storage and supply^{6,7}. The key point of the Sabatier reaction is the activation of stable O = C = O molecules, which have a high bonding energy of 806 kJ mol⁻¹, for hydrogenation toward the production of methane^{8,9}. However, most conventional catalysts require high temperatures (300-400 °C) to achieve reliable CO₂ conversion and are subject to deactivation and production cost issues¹⁰⁻¹².

A low oxidation state Ru species was recently reported as a catalyst for low-temperature CO₂ methanation^{13,14}. Carbon compounds or doping in the Ru species played a crucial role in the stabilization of low oxidation state Ru and provided abundant Lewis active sites for the activation of CO₂. Nevertheless, the bottleneck for these catalysts was that high temperature (\geq 180 °C) and high pressure (20 bar) were necessary to prevent reduction of the low oxidation state of the Ru species.

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Here, a new strategy to stabilize the low oxidation state Ru is proposed by a simple ion-exchange method. Layered Na₂Ti₃O₇-supported Ru catalyst (denoted Ru_xTi_yO_z) was prepared by the ion exchange of Na₂Ti₃O₇ with the adjustment of various synthesis conditions. The negatively charged (Ti₃O₇)² layers feasibly uptake and well distribute Ru ion, stabilizing the low oxidation state Ru under the reaction conditions, even at ambient pressure. Ru_xTi_yO_z exhibited significantly low-temperature activity (\geq 140 °C) with a reliable conversion rate and 100% CH₄ selectivity, which was 9.7-102 times higher activity than commercial and state-of-the-art catalysts. Moreover, Ru_xTi_yO_z was also successfully synthesized at the gram scale and on a 3D-printed metal self-catalytic reactor, which indicates the superior scalability of this approach to move beyond the lab scale.

Results

Synthesis and characterization of Ru_xTi_yO_z

Rux TivOz was synthesized via the simple ion exchange of Na2Ti3Oz with RuCl₃ xH₂O as a precursor (Fig. 1a). The pH, temperature, and precursor concentration are crucial factors in the ion-exchange process that affect the exchange behavior: therefore optimization of the synthesis process was investigated through the use of various conditions (see Supplementary Figs. S1-7, and Tables S1-2). Ion exchange at 160 °C resulted in the highest amount of Ru uptake and was thus confirmed as the optimum condition for catalytic application. X-ray diffraction (XRD) measurements showed a significant peak shift to higher angles with a decrease in the intensity, which implied the ion exchange of large ionic radius Na⁺ (1.02 Å) with smaller Ru³⁺ (0.68 Å) or Ru^{4+} (0.62 Å) (Fig. 1b)¹⁵. A peak from 10.54° to 11.14° indicated the shrinkage of the interlayer from 8.39 Å to 7.93 Å due to Ru ion exchange, which further supported the existence of Ru within the layered structure¹⁶. Furthermore, Le Bail fitting of XRD patterns showed a change of space group from P2m to C2m with lattice distortion due to the high charge number of Ru ions compared with the Na₂Ti₃O₇ (JCPDS card No. 31-1329) and H₂Ti₃O₇ (JCPDS card No.47-0561) phases, which indicates that Ru exist between interlayer bonding with the $(Ti_3O_7)^2$ octahedron layer (Supplementary Fig. S8-10, and Table S4). RuO₂ (JCPDS No. 43-1027) was also identified as an inevitable precipitant due to an abrupt change of the local pH by hydrolyzed OH⁻ formed by charge compensation of ion-exchanged Na⁺¹⁷. Scanning transmission electron microscopy (STEM) observations of fresh $Ru_xTi_yO_z$ samples showed there was a mixture of two separate phases, nanoporous RuO₂ and Ru_xTi_yO_z (Fig. 1c, Supplementary Figs. S11-13, and Table S5). The majority of nanoporous RuO₂ was present as a form of aggregated precipitant, and some of the nanoporous RuO₂ was supported on the crystallized $Ru_xTi_yO_z$ (Supplementary Fig. S13-15). Figure 1d shows a selected area electron diffraction (SAED) pattern of $Ru_{x}Ti_{y}O_{z}$ along the [111] direction with clear streaking of diffraction spots along the c*-axis. These spots resulted from the assembly of aperiodic stacking faults or a disordered layer structure caused by the Ru cation, which further supports the presence of Ru species between the layer structure^{18,19}.

To investigate the hyperfine structure of the $Ru_xTi_yO_z$ catalyst, high-angle annular dark-field STEM (HAADF-STEM) and X-ray absorption spectroscopy (XAS) measurements were performed. HAADF-STEM/EDS images indicated that the fresh sample consisted of a mixture of $Ru_xTi_yO_z$ and RuO_2 (Fig. 2a and Supplementary Figs. S15 and S16). EDS elemental mapping confirmed Ru species were highly dispersed over the $Ru_xTi_yO_z$ by the ion exchange process. X-ray adsorption near-edge spectroscopy (XANES) showed a similar average charge state that was located close to Ru^{4+} (Fig. 2b). These results were reasonable because the commercial hydrate ruthenium chloride ($RuCl_3$ ·xH₂O), that was used as a precursor in this study is mostly composed of ruthenium oxychloride (Ru_2OCl_6 , Ru(IV))²⁰. Moreover, the small ionic radius and high valence Ru^{4+} (0.62 Å) were preferentially ion-exchanged into the layered structure rather than $Ru^{3+}(0.68 Å)^{15,16}$. The Fourier-transformed extended X-ray absorption



Fig. 1 | Synthesis of Ru_zTi_yO_z. a Schematic illustration of the ion exchange of Na₂Ti₃O₇ to Ru_xTi_yO_z. Atomic structures were visualized using VESTA³⁶. b XRD patterns of Na₂Ti₃O₇ and Ru_xTi_yO_z catalysts. c Low magnification HAADF-STEM image of fresh Ru_xTi_yO_z. d SAED pattern along the $[1\overline{11}]$ zone axis.



Fig. 2 | Nanoscopic characterization of Ru₂Ti₂O₂. a High magnification HAADF-STEM and EDS image of fresh Ru_xTi₂O₂. b Ru K-edge XANES spectra of fresh Ru_xTi₂O₂ with RuO₂, RuCl₃, and Ru foil as references. c Ru K-edge FT-EXAFS spectra of fresh Ru_xTi₂O₂ and references. d WT.-EXAFS spectra of Ru foil, RuO₂, and Ru_xTi₂O₂.

fine structure (FT-EXAFS) spectrum of Ru_xTi_yO_z also showed a predominant peak of Ru-O on the first shell at 1.5 Å, which was attributed to atomically distributed Ru in the interlayer structure and minor peaks of Ru-O-Ti (Ru) on a second shell in 2-4 Å from the overlapping of the scattering of Ti and precipitated RuO₂ without RuCl₃ and metallic Ru (Fig. 2c and Supplementary Figs. S17 and S18)^{21,22}. Wavelet transform (WT) of EXAFS (Fig. S6) provided more local geometric information for Ru_xTi_yO_z (Fig. 2d). The strong scattering for the lower radial distance is associated with Ru-O (4-8 Å⁻¹, 1-2 Å) and the resolved second scattering between interlayer Ru-O-Ti (6-8 Å⁻¹, 2.5-3.0 Å) and the surfaceadsorbed Ru and Ti²³. The remaining peaks were due to the scattering by Ru-O-Ru in the precipitated RuO₂, in accordance with the STEM results.

Evaluation of the catalytic performance of Ru_xTi_yO_z

To evaluate the performance of as-synthesized Ru_xTi_vO_z for CO₂ methanation, catalytic tests were conducted using the conditions H₂:CO₂ = 3, CO₂ = 23.75%, 24,000 mL g_{cat}^{-1} h⁻¹, and atmospheric pressure (1 bar). RuxTivOz began to exhibit an adequate CO2 conversion rate from 100 °C and reached 14% conversion with 100% methane selectivity at 140 °C, which is equivalent to a methane space-time yield (STY_{CH4}) of 0.0326 mol g_{cat}^{-1} h⁻¹. Multiple Ru reference catalysts were prepared to precisely evaluate the performance of RuxTivOz. Figure 3a shows results for the CO₂ methanation performance at 140 °C for the various reference catalysts. Compared with conventional Ru catalysts (Ru black, Ru/Al₂O₃ (5 wt.%), and Ru/TiO₂ (8 wt.%) and a recently reported state-of-the-catalyst (RuO₂/C, 75 wt.% RuO₂), Ru_xTi_vO_z showed at least 9.7 and up to 102.4 times higher catalytic performance. These values represent, to the best of our knowledge, outstanding performance compared with reported state-of-the-art catalysts for CO₂ methanation (Supplementary Table S6).

In addition to the high activity, long-term stability is a crucial factor that should be accomplished for scale-up and industrial application of the catalyst (Fig. 3b). Therefore, the long-term stability of $Ru_xTi_yO_z$ was examined at 140 and 180 °C. After 80 h of long-term testing at 140 °C, the catalytic activity was maintained at 11% conversion with 100% methane selectivity, which corresponds to a STY_{CH4} of 0.026 mol g_{cat}^{-1} h⁻¹. Furthermore, long-term stability tests at 180 °C

showed Ru_xTi_yO_z was stable for 220 h of continuous reaction with the high conversion rate (ca. 56%) preserved with 99.99% methane selectivity and an STY_{CH4} of 0.131 mol g_{cat}^{-1} h⁻¹. However, a further increase in the reaction temperature to 300 °C rapidly deactivated the catalyst, and a 19.8% decrease in activity was observed after the initial 5 h of reaction (Supplementary Fig. S19).

In the P2G scenario, the intermittency of renewable energy is a critical drawback: therefore, maintenance of the performance over the periodic fluctuation of a reaction condition is an important aspect. We designed a temperature-controlled intermittency test combined with a power on-off method that included a harsh off condition; a decrease in temperature to 20 °C and exposure to N2 gas for 12 h. For initial exposure at 140 °C, the activity of RuxTivOz was recuperated with a conversion rate loss of 4% for 4 successive on-off rounds (Fig. 3c). The temperature was subsequently increased to 180 °C, whereby a conversion rate of 57.8% was achieved, which was only 2% different to that for the fresh catalyst. However, after exposure of the catalyst at 180 °C, the conversion rate at 140 °C suddenly decreased by 4% compared with the previous round, which implied a significant loss of active sites after exposure to 180 °C. Despite a certain amount of activity loss, the catalytic performance was well preserved over 3 rounds of the 140-180 °C step-switching intermittency test. Afterward, the reaction temperature was increased to 300 °C after the 180 °C reaction. Following exposure to 300 °C, the activity was observed to decrease by 2.1% and 16.5% at 140 °C and 180 °C, respectively, representing only 15% and 27% of the activity obtained in the fresh sample.

Deactivation of the catalyst was observed after exposure to temperatures of 180 and 300 °C; therefore, XRD patterns for the used samples were obtained to investigate the phase transition under the reaction conditions (Supplementary Fig. S20). After exposing the catalyst under the reaction condition, RuO_2 peaks disappeared with the emerging of Ru^0 peaks, indicating the formation of Ru nanoparticles. Nevertheless, unlike at 140 °C, variation of the layered structure was observed from 180 °C. This was attributed to partial reduction and a decrease of interlayer Ru^{4+} causing a slip of the Ti-O octahedra layer structure along the [$\bar{1}53$] facet and transformation of the layer structure to a structure similar to $Na_2Ti_6O_{13}^{24}$. However, an increase in temperature to 300 °C caused the layer structure to



Fig. 3 | **Catalytic performance of Ru**_z**Ti**_y**O**_z. **a** CO₂ methanation performance for various commercial and state-of-the-art Ru catalysts. Reaction conditions: T = 140 °C, P = 1 bar, GHSV = 24000 mL g_{cat}⁻¹ h⁻¹. **b** Long-term stability tests of Ru_x**Ti**_yO_z at 140 and 180 °C. Reaction conditions: P = 1 bar, GHSV = 24000 mL g_{cat}⁻¹ h⁻¹. **c** Intermittency tests with the variation of the reaction temperature. Reaction

conditions: P = 1 bar, GHSV = 24000 mL g_{cat}^{-1} h⁻¹. **d** CO₂ methanation performance after annealing and reaction. Reaction conditions: = 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.

structure; a detailed characterization of the catalyst samples is given in

collapse and exfoliate to TiO₂ because the interlayer Ru species was fully reduced, which was confirmed by hydrogen temperature programmed reduction (H₂-TPR) measurements (Supplementary Fig. S21). Therefore, preservation of the layered Ru_xTi_yO_z structure was confirmed to be a key point to retain the catalytic performance.

The importance of the layered $Ru_xTi_yO_z$ structure was further supported by activity tests performed after heat treatments selected according to TGA. (Supplementary Fig. S22). Elevation of the treatment temperature in N₂ transformed the layered $Ru_xTi_yO_z$ into A-TiO₂ and R-TiO₂ from 300 °C along with the disappearance of the layered structure (Supplementary Fig. S23). In addition, the deactivation of the catalyst exhibited a linear tendency with the disappearance of the layer structure caused by increasing temperature. (Fig. 3d). After heat treatment at 300, 500, and 800 °C in N₂, the conversion rate decreased by 50, 91.6, and 96.1%, respectively. Moreover, the sample treated in H₂ at 300 °C lost 80.9% of activity, which was 30.9% more than the N₂treated sample. This indicated that the layered structure played a crucial role in the low-temperature CO₂ methanation (Supplementary Fig. S24 and S25).

In summary, we have confirmed the outstanding catalytic performance of layered $Ru_xTi_yO_z$, at low temperature, and its high robustness during long-term and intermittency tests. There was significant deactivation of the catalyst with the destruction of the layer

was con- Characterization of used Ru_xTi_yO_z Figure 4a showed the HAADF-STEM/EDS results for a catalyst sample

the next chapter.

used at 140 °C. The morphology of the used sample was similar to the as-synthesized sample consisting of two separate phases, i.e., aggregated Ru and atomically distributed Ru with Ti and O (Supplementary Figs. S26–28). The former consisted of metallic Ru nanoparticles due to the reduction of precipitated RuO₂, while the latter was atomically distributed Ru species of $Ru_xTi_yO_z$ with high dispersion maintained, even after exposure to the reaction conditions. The streaking of diffraction spots in the [110] SAED pattern implied the preservation of Ru ions within the disordered layer structure (Supplementary Fig. S28).

In-situ XAS was conducted to reflect the variation of $Ru_xTi_yO_z$ under the various reaction conditions. The temperature was first ramped to 140 °C and maintained for 2 h (Fig. 4b and Supplementary Fig. S29, S30). In the initial period, exposure to reducing conditions resulted in an instantaneous diminishment of the second shell (2-4 Å) peaks due to the preferential reduction of nanoporous RuO_2 to Runanoparticles, whereas strong first shell Ru-O bonds (ca. 2 Å) attributed to $Ru_xTi_yO_z$ remained with the appearance of Ru-Ru (2.67 Å) bonds from the formation of Ru particles. Linear combination fitting



Fig. 4 | **Characterization of used Ru**_z**Ti**_y**O**_z. a STEM-EDS images of Ru_x**Ti**_y**O**_z after the reaction at 140 °C. **b** FT-EXAFS spectra of fresh and used Ru_x**Ti**_y**O**_z samples at Ru K-edges. **c** Ru 3 d XPS spectra of fresh and used Ru_x**Ti**_y**O**_z samples. **d** In-situ XRD

spectra of $Ru_x Ti_y O_z$ collected during the reaction with increasing temperature and time. Atomic structures were visualized using VESTA³⁶. **e** EPR spectra of fresh and used $Ru_x Ti_y O_z$ samples and used RuO_2 sample as reference.

indicated the in-situ reduction of Ru_xTi_yO₇ was stabilized after 1 h and 21.6% of the Ru oxide remained after 2 h (Supplementary Fig. S30). There was not only a decrease in the Ru-O intensity, but also a significant shift of the Ru-O peak position during the reaction, which indicated the in-situ transformation of the local geometric structure of RuxTivOz. Based on FT-EXAFS curve fitting, the average Ru-O coordination number (CN) after the reaction at 140 °C decreased from 5.75 to 2.46 with an increase in the CN of metallic Ru-Ru to 6.18, and the bond length of Ru-O was also elongated from 1.98 Å to 2.03 Å (Supplementary Fig. S31 and Table S7). In-situ synchrotron XRD measurements of the sample at 140 °C showed a peak shift, especially (200) peaks, which represented a shift from 11.14° to 11.12° and expansion of the interlayer distance from 7.930 Å to 7.949 Å, even maintaining its structure in the ex-situ conditions (Fig. 4c and Supplementary Fig. S32-36). Combined with the results of in-situ characterization, this phenomenon was attributed to the variation of the RuO₆ group between layered Ru_xTi_yO₇ under the reducing conditions. The partial reduction of Ru⁴⁺ to a low oxidation state Ru species resulted in layer expansion due to the large ionic radius of the low oxidation state Ru species, i.e. Ru⁴⁺ (0.62 Å) to Ru³⁺ (0.68 Å), accompanied by lowering of the coordination number resulting from a decrease in the charge density of Ru. The generation of low oxidation state Ru species by reduction was further confirmed by electron paramagnetic resonance (EPR) and XPS measurements. Although the Ru^{4+} (4 d^4) and Ru^0 species have a non-Kramers nature (EPR-silent), Ru^{3+} (4 d^5) was an EPR-sensitive species due to the single unpaired electron (s = 1/2); therefore, it was possible to observe an EPR signal²⁵. After reaction at 140 °C, the sample showed the emergence of intense signals of $g_{s1} = 2.17$, $g_{s2} = 2.08$, and $g_{s3} = 1.95$ attributed to the Ru³⁺ species, which were not evident when RuO₂ was used under the same reaction conditions (Fig. 4d)²⁶. The low-intensity

signal at $g_c = 2.00$ assigned to oxygen vacancies (O_v) may be due to RuO_x formed over reduced Ru nanoparticles during exposure to air, which was in accordance with the signal of the used RuO_2 sample. The XPS results also clearly indicated a shift of the Ru $3d_{5/2}$ peak to lower binding energy after exposing the fresh sample to the reaction condition at 140 °C (Fig. 4c). Unlike the fresh sample, which consisted of Ru⁴⁺ species, the spectrum of the sample exposed to 140 °C showed a split to Ru⁴⁺ (280.8 eV), Ruⁿ⁺ ($1 \le n \le 3$, 280.2 eV), and Ru⁰ (279.8 eV) with the proportion of 46.4% of Ruⁿ⁺, which indicated the generation of a low oxidation state Ru species during the 140 °C reaction^{13,27}.

The increase of the reaction temperature to 300 °C gradually reduced the Ru oxide species, which was fully reduced to metallic Ru around 300 °C (Fig. 4b, e and Supplementary Fig. S37). In XPS spectra after the reaction at 180 °C and 300 °C, the Ru oxide signal was diminished and a strong Ru⁰ (279.8 eV) signal emerged due to Ru nanoparticles (Fig. 4e, Supplementary Fig. S38, and Table S8). The EPR spectrum of the 300 °C sample showed the complete disappearance of Ru³⁺ species and the emergence of strong peaks at $g_b = 2.04$ and $g_c = 2.00$, which were assigned to dissociative O⁻ and oxygen vacancy (O_v), respectively⁸. This was due to the collapse of the layered structure by the complete reduction of low oxidation Ru species and exfoliation to produce TiO₂, similar to the spectrum for a conventional supported Ru/TiO₂ catalyst²⁸.

The generation of low oxidation state Ru species was thus confirmed, which had a critical relationship with the catalytic performance. These low oxidation state Ru species were considered to provide Lewis active sites at not only the interface of $Ru^{n+} - (Ti_3O_7)^{2^\circ}$ but also electron-deficient Ru^{n+} as a form of coordination activation, facilitating CO₂ adsorption which is known as the rate-determining step^{13,29}. From CO₂-TPD results,



Fig. 5 | Characterization of used Ru_xTi_yO_z. a CO₂-TPD profiles of Ru_xTi_yO_z after reaction at 140, 180, and 300 °C. b Relative CO₂ adsorption capacity obtained from CO₂-TPD. c H₂-TPR profiles after reduction at 140, 180, and 300 °C in H₂.

the CO₂ adsorption capacity was decreased from 84.7% and 36.2% at 180 °C and 300 °C, respectively, compared to 140°C, and the desorption peak shifted to high temperature $(300 \rightarrow 400 \text{ °C})$ as with that for the conventional supported Ru/TiO₂ catalyst (Fig. 5a, b and Supplementary Fig. S39). H₂-TPR results also showed the proportional disappearance of the H₂ consumption peak with higher reaction temperature, which implied a reduction of low oxidation state Ru sites to metallic Ru and the loss of active sites for CO₂ adsorption (Fig. 5c). H₂-D₂ isotopic exchange experiments were also conducted because the activation of hydrogen is also an important factor for CO₂ hydrogenation (Supplementary Fig. S40 and S41)³⁰. Even though the formation of Ru⁰ nanoparticles promoted hydrogen activation in the initial step, no significant difference in activation ability between the 140 and 300 °C samples indicated that hydrogen activation was not the rate-determining step in this catalyst.

Various reference catalyst substitutes from Na₂Ti₃O₇ were synthesized under the same conditions with the same or even higher contents of Ru (Supplementary Fig. S25). The results showed that none of these catalysts could activate CO₂ at low temperature, which supports the importance of the low oxidation state Ru species on the layered Ru_xTi_yO_z structure.

Scalability of Ru_xTi_yO_z

The scalability of a catalyst is one of the crucial aspects of the catalyst development process to move beyond the lab-scale to industrial-scale applications^{31,32}. Therefore, the synthesis of $Ru_xTi_yO_z$ was scaled up from the milligram (mg) scale to the gram (g) scale. In the milligram scale synthesis, 0.11 g of the catalyst was synthesized, whereas 2.02 g of the catalyst was successfully synthesized at once in the gram scale (Fig. 6a and Supplementary Fig. S42). The catalytic performance at the milligram and gram scales as a function of temperature were less than ±5% of each other, which indicates the superior scalable properties of Ru_xTi_yO_z based on the facile ion exchange synthesis method (Supplementary Fig. S43). As a new method to scale up, a Ti alloy 3D-printed metal self-catalytic reactor (3D SCR) with a honeycomb shape was fabricated using the laser beam-powder bed fusion (L-PBF) technique (Supplementary Figs. S44, S45 and Table S9). The 3D SCR integrated both the functions of catalyst and reactor is thus expected to be a shortcut to scale up by minimizing the catalyst development process and utilizing the advantages of 3D printing, such as customization and compaction³³⁻³⁵. A double-step hydrothermal process was conducted to form Na_xH_{2-x}Ti₃O₇ nanorods as a precursor of Ru_xTi_vO_z on the Ti alloy 3D SCR (Fig. 6b and Supplementary Figs. S46, S47). Na_{2-x}H_xTi₃O₇ was then ion-exchanged to Ru_xTi_yO_z through the ion-exchange process. SEM/EDS results and XRD patterns showed the transformation of TiO_2 into $Na_xH_{2-x}Ti_3O_7$ and the formation of $Ru_xTi_yO_7$ nanorods on the 3D SCR along with each step (Fig. 6c, d and Supplementary Figs. S4850). The catalytic activity of $Ru_xTi_yO_z/Ti$ SCR was also superior at low temperature and exceeded the performance of the milligram scale (Fig. 6e). Therefore, the ion-exchange method could provide a new method for the surface treatment and break through the obstacle of nanoscopic functionalization of a 3D SCR.

Discussion

In summary, layered Na₂Ti₃O₇-supported Ru catalyst was successfully prepared by a facile ion-exchange method as a highly active-robust catalyst for low-temperature CO₂ methanation. The negatively charged $(Ti_3O_7)^{2^{-}}$ layer facilitated the generation and stabilization of the low oxidation state Ruⁿ⁺ species for the activation of CO₂ under mild conditions at atmospheric pressure (1 bar). The simple ion exchange process also allowed for scale-up and the nanoscopic surface functionalization of layered structures as active sites for catalytic reactions.

Methods

Synthesis of Ru_xTi_yO_z

Ru_xTi_yO_z was synthesized by an ion exchange process. Details of the synthesis process are given in the Supplementary Information. As an optimum condition, 0.10501g of NaHCO₃ was dissolved in 25 mL of deionized water and stirred for 30 min at room temperature. 0.11554 g of RuCl₃·xH₂O was dissolved with vigorous stirring until no CO₂ bubbles were generated and then 0.1g of Na₂Ti₃O₇ was added to the solution. Lastly, the solution was sealed in a stainless-steel autoclave and hydrothermally treated with vigorous stirring at 160 °C for 24 h. The solution was cooled to room temperature and filtrated with sufficient water and then dried at 100 °C for 6 h. In the case of the gram scale synthesis of Ru_xTi_yO_z, the solution was prepared with 1.5751g of NaHCO₃, 1.7331g of RuCl₃·xH₂O, and 1.5g of Na₂Ti₃O₇ dissolved in 350 mL of deionized water and with the same synthesis conditions.

Characterization of catalysts

Details of all characterization methods are given in the Supplementary Information.

Evaluation of catalytic performance

The CO₂methanation performance was evaluated using a fixedbed reactor system. Powder samples (50 mg) were placed into a U-shaped quartz cell with an internal diameter of 10 mm and a catalyst bed height of 0.5 mm, without shaping the catalyst, and then placed in an electric oven. In the case of the 3D SCR, the reactor was placed in the middle of a quartz cell held within a ribbon heater (Supplementary Fig. S50). All samples were tested without pretreatment. The supported Ru/TiO₂ and Ru/TiO₂ (3D



Fig. 6 | **Scale-up of Ru_zTi_yO_z. a** Photograph of milligram and gram scale synthesized Ru_zTi_yO_z. **b** Photograph of as-printed, oxidized, as-synthesized Na_xH_{2-x}Ti₃O₇, and Ru_xTi_yO_z on the 3D Ti SCR. **c** Low and high magnification SEM images of Ru_xTi_yO_z on the 3D Ti SCR. **d** XRD patterns of as-synthesized Na_xH_{2-x}Ti₃O₇ and

 $Ru_xTi_yO_z$ on the 3D Ti SCR. **e** Temperature-dependent CO₂ conversion with reference, milligram, gram scale samples, and $Ru_xTi_yO_z/Ti$ SCR. Reaction conditions: P = 1 bar, GHSV = 24000 mL g_{cat}^{-1} h⁻¹.

SCR) catalysts as reference samples were reduced in a H_2 flow at a flow rate of 40 mL min⁻¹ at 300 °C for 2 h. The methanation of CO₂ was conducted with a mixed feed gas ($H_2/CO_2/N_2 = 71.25:23.75:5$) at a flow rate of 20 mL min⁻¹. The performance was obtained when the conversion and selectivity reached a steady state for three successive measurements. The gas products were analyzed using an online gas chromatograph (Shimadzu GC–14B) equipped with an active carbon column connected to a flame ionization detector combined with a methanizer. The conversion and selectivity were calculated as follows:

$$CO_{2_{conversion}}(\%) = \frac{CO_{2_{in}} - CO_{2_{out}}}{CO_{2_{in}}} \times 100\%$$
 (1)

$$CH_{4_{selectivity}}(\%) = \frac{CO_{4_{out}}}{CO_{2_{in}} - CO_{2_{out}}} \times 100\%$$
(2)

Fabrication of Ti 3D SCR and Ru_xTi_yO_z/Ti SCR

Ti-6Al-4V powder (EOS, Krailling, Germany) prepared by a gasatomization process was used as a starting material. EOS M 290 (EOS, Krailling, Germany) was used for L-PBF, and a cylinder-shaped 3D reactor with a 23 mm diameter and a length of 70 mm was fabricated using an XY scan strategy. The building platform was heated to 80 °C, and the O₂ concentration was maintained at less than 100 ppm by an Ar gas purge. The laser power (P) was 250 W, the scan speed (v) was 1200 mm, the hatch distance (d) was 0.1, and the layer thickness (t) was 0.06 mm.

The as-printed Ti 3D SCR was sonicated in acetone for 15 min and dried in an oven at 100 °C for 3 h. The Ti 3D SCR was then oxidized in a furnace at 750 °C for 6 h at a ramp rate of 10 °C min⁻¹. The oxidized Ti 3D SCR was placed in the center of a Teflon rack in a Teflon liner filled with 350 mL of 10 M NaOH and sealed in a stainless autoclave. The autoclave was placed in an oven and hydrothermal treatment was performed at 210 °C for 8 h. The resultant $Na_xH_{2-x}Ti_3O_7/Ti$ 3D SCR was washed using deionized water until the pH reached 11 and was then dried at 100 °C overnight. For the ion-exchange process, the Na_xH_{2-x}Ti₃O₇/Ti 3D SCR was placed in the center of a Teflon rack in a Teflon liner filled with 350 mL of a solution with 1.0501 g of NaHCO₃ and 1.1554 g of RuCl₃·xH₂O, and then sealed in a stainless autoclave. The autoclave was hydrothermally treated with vigorous stirring at 120 °C for 24 h. The ion exchange process of the Ti 3D SCR was repeated three times to ensure the saturation of Na_xH_{2-x}Ti₃O₇ on the Ti 3D SCR.

Data availability

All data generated during this study are included in this article and its Supplementary Information or are available from the corresponding authors upon request.

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Author contributions

H.K performed the sample preparation, calculation, and characterization, and wrote the manuscript with help from K.M. K.M. supervised all of the project and provided funding. S.I. obtained HR-TEM images. T.N. helped with the preparation of metal 3D printed reactor. H.Y. helped supervise the project. The manuscript was written through the discussion with all authors. All authors have given approval to the final version of manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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