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# TiH<sub>2</sub>-supported Ru catalyst with unusual electron transfer behaviour for highly efficient carbon dioxide methanation at low temperature

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Catalytic CO<sub>2</sub> methanation is of particular significance and growing interest due to its applications in many important industrial fields. The development of advanced heterogeneous catalysts for CO<sub>2</sub> methanation depends predominantly on the rational regulation of metal-support interaction (MSI), which remains challenging despite of recent progress. Here, we develop a new heterogeneous catalyst of TiH<sub>2</sub>-supported Ru nanoparticles (NPs), which feature notable electron transfer from TiH<sub>2</sub> support to Ru NPs and enhanced capability of CO intermediate activation for CO<sub>2</sub> methanation, distinct from TiO<sub>2</sub>supported Ru catalysts synthesized under similar mild conditions. The electron transfer behavior and hydrogen spillover effect in TiH<sub>2</sub>-supported Ru NPs (denoted as RTH) are optimized at a moderate Ru loading of 9.8 wt.% in 100RTH, where the impacts of Ru loading on CO intermediate activation, H<sub>2</sub> activation and catalyst surface hydration are synergistically balanced. When evaluated at 200 °C under 4 bar pressure, 100RTH delivers a notable CH<sub>4</sub> selectivity of 99.8% and a superior CH<sub>4</sub> production rate of 168.7 mmol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup>, which is 21.1 times more active than pure Ru NPs. Our work provides valuable insights into the MSI-directed development of heterogeneous catalysts for highly efficient CO<sub>2</sub> conversion and utilization.

# Introduction

The excess emission of carbon dioxide (CO<sub>2</sub>), the primary greenhouse gas, have caused challenging issues including global warming, biological system imbalances, and ocean acidification in the past decades.<sup>1, 2</sup> It is therefore highly desirable to develop capable technology and devices for efficient capture, utilization, and storage of CO<sub>2</sub>. As a promising strategy to achieve net-zero emission fuel cycle, catalytic CO<sub>2</sub> hydrogenation have attracted extensive interest, since it allows the conversion of CO<sub>2</sub> into various value-added chemicals such as CO, CH<sub>4</sub>, CH<sub>3</sub>OH, HCOOH, and other hydrocarbons.<sup>2, 3</sup> The catalytic hydrogeneration of CO2 to produce CH4 (known as CO2 methanation or Sabatier reaction) are of particular significance and growing interest in recent years, which has found applications in several important industrial fields including the production of synthetic nature gas and the hydrogen feedstock purification for ammonia production.<sup>4, 5</sup> Due to the strong C=O double bonds of CO<sub>2</sub> (bond energy of 750 kJ mol<sup>-1</sup>),<sup>6</sup> CO<sub>2</sub> methanation process is usually operated at high temperature (>300 °C) and in the presence of heterogeneous catalysts. Typical heterogeneous catalysts for CO<sub>2</sub> methanation are highly active metal nanoparticles (NPs; such as Ru, Rh, Co, and Ni<sup>7-14</sup>) supported on reducible oxide supports (like TiO<sub>2</sub>, CeO<sub>2</sub>, and ZrO<sub>2</sub><sup>7, 8, 13, 15, 16</sup>) that anchor metallic NPs and prevent NPs from agglomeration at high reaction temperature. For such heterogeneous catalysts, the metal–support interaction (MSI) has a critical impact on the physiochemical properties of catalysts and the catalytic hydrogeneration process.<sup>17, 18</sup> Rational MSI regulation thus has been widely used as a predominant strategy to achieve excellent catalytic performance (activity, selectivity, and stability) for CO<sub>2</sub> hydrogeneration.

Typical MSI operating in catalytic CO<sub>2</sub> hydrogeneration includes electron transfer, strong metal-support interaction (SMSI), and hydrogen spillover.<sup>7</sup> Taking supported Ru catalyst, one of the most efficient heterogeneous catalysts towards CO2 hydrogeneration, for an example, recent studies reveal that the support-metal electron transfer plays a crucial role in the product selectivity, by impacting on the adsorption and activation of CO intermediates.<sup>16, 19, 20</sup> Due to the partially positive charge on the C atoms of C=O bonds in CO intermediates, electron transfer from Ru to TiO<sub>2</sub> decreases the electron density around Ru NPs and thus moderately weakens the adsorption and subsequent activation of CO intermediates on Ru, leading to high CO selectivity over CH<sub>4</sub>.<sup>20</sup> In contrast, electron transfer from CeO<sub>2</sub> support to Ru increases the electron density around Ru NPs, which facilitates the adsorption and activation of CO intermediates and in turn results in 100% CH<sub>4</sub> selectivity.<sup>16</sup> SMSI is usually observed when reducible oxides (e.g., TiO<sub>2</sub>) are used as support for metal NPs and (partially) reduced at high temperature (300-700 °C) under

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reducing atmosphere (typically,  $H_2$ ) or ultrahigh vacuum, leading to the migration of support to metal NP surface and the subsequent formation of an oxide overlayer around metal NPs.<sup>9</sup>, <sup>21</sup> For TiO<sub>2</sub>-supported Ru catalysts, SMSI generally results in deteriorative activity but enhanced stability of Ru NPs due to the coverage of their surface sites by TiO<sub>2</sub> overlayer.<sup>7</sup> Moreover, due to the higher Fermi lever of partially reduced TiO<sub>2</sub> support as compared with Ru NPs, SMSI induces electron transfer from TiO<sub>2</sub> support to Ru NPs and thus results in high CH<sub>4</sub> selectivity,<sup>7</sup>, <sup>22, 23</sup> in sharp contrast to TiO<sub>2</sub>-supported Ru catalysts prepared under mild conditions (e.g., wet impregnation method), in which the electron transfer from Ru to TiO<sub>2</sub> leads to high CO selectivity.<sup>20</sup>

Hydrogen spillover also readily occurs when reducible oxide supported metal NP catalysts are used for CO<sub>2</sub> hydrogenation. Hydrogen spillover benefits the activation of H<sub>2</sub>, since abundant, highly active hydrogen atoms can be generated by the dissociative adsorption of H<sub>2</sub> on metal NP surfaces and the spontaneous migration of hydrogen atoms to the surface of reducible oxide support.<sup>21</sup> Therefore, hydrogen spillover has been been utilized to improve the activity of supported catalysts towards CO<sub>2</sub> hydrogenation. However, recent study based on CeO2-supported Ru catalysts reveals that hydrogen spillover should be regulated at an appropriate level to suppress the adverse hydration of catalyst surfaces, and also to achieve a balance with SMSI due to their competitive relationship.<sup>16</sup> Given the critical and complex roles of MSI in the performances of supported catalysts, the rational regulation of MSI is therefore of notable significance for highly efficient CO<sub>2</sub> methanation, which remains very challenging despite recent progresses.<sup>17, 24</sup>

Here, we develop a new heterogeneous catalyst for CO<sub>2</sub> methanation, by utilizing TiH<sub>2</sub> as the support for Ru NPs. TiH<sub>2</sub>supported Ru NPs (denoted as mRTH, in which m refers to the mass loading of RuCl<sub>3</sub> precursor in mg) can be readily prepared in solution by the deposition of Ru NPs on TiH<sub>2</sub>. Benefitting from the highly active, negatively charged hydrogen species of H<sup>-</sup> in TiH<sub>2</sub>, spontaneous oxidation of TiH<sub>2</sub> surface occurs under ambient conditions,<sup>25</sup> leading to the formation of a thin surface layer of oxides and oxyhydrides (denoted as TiO<sub>x</sub>H<sub>y</sub>) between bulk TiH<sub>2</sub> and Ru NPs. The TiO<sub>x</sub>H<sub>y</sub> surface layer acts as partially reduced oxide support for Ru NPs and enables notable electron transfer from support to Ru NPs, which thus remarkably enhances the activation of CO intermediates on Ru NPs, and in turn results in superior activity and CH<sub>4</sub> selectivity towards catalytic CO<sub>2</sub> methanation. Despite similar electron transfer behaviour observed in SMSI-mediated TiO<sub>2</sub>-supported Ru catalysts, the TiH<sub>2</sub>-supported Ru NPs do not require reduction treatment at very high temperature (300-700 °C), and thus avoids the formation of adverse oxide overlayer on Ru NPs that impairs the catalytic activity and/or selectivity of Ru NPs. Moreover, such electron transfer behaviour has not been observed in traditional TiO<sub>2</sub>-supported Ru catalysts synthesized under similar mild conditions, in which the electron transfer from Ru to TiO<sub>2</sub> results in high CO selectivity. Additionally, the electron transfer is appropriately coupled with hydrogen spillover effect to achieve synergistic balance between CO activation, H<sub>2</sub> activation and catalyst surface hydration, which

finally imparts superior activity and  $CH_4$  selectivity to  $TiH_2$ -supported Ru NPs for catalytic  $CO_2$  methanation.

## Experimental

#### Chemicals

Ruthenium trichloride (RuCl<sub>3</sub>) was purchased from Bide Pharmatech Ltd. Titanium hydride (TiH<sub>2</sub>, 95%; >99% Ti) was purchased from Strem Chemicals Inc. Ethyl Glycol (99.5%) was purchased from Titan Scientific Company Ltd, Shanghai. Millipore deionized water (18.2 M $\Omega$ ·cm) was used for solution preparation. All reagents were used as received unless otherwise noted.

#### Synthesis of mRTH (m = 50, 100, 150, and 200)

TiH<sub>2</sub> powder (200 mg) was added to a round bottom flask (100 mL) with ethylene glycol (EG; 25 mL) and deionized water (25 mL), and treated with ultrasonication and vigorous stirring for 15 min. Then RuCl<sub>3</sub> (50 mg) were added to the solution, and treated with ultrasonication and vigorous stirring for 60 min. Subsequently, the obtained brownish-black solution was heated at 150 °C with an oil bath for 180 min, and allowed to cool down to room temperature under ambient condition. The product, denoted as 50RTH, was collected by centrifugation and washed with water and ethanol three times. The synthesis of other samples of 100RTH, 150RTH, and 200RTH was achieved by changing the mass of RuCl<sub>3</sub> while keeping all the other parameters unchanged.

#### Synthesis of Ru NPs

The synthesis of Ru NPs (as control sample) was accomplished by following the same procedure for the synthesis of Ru NPs described above. Briefly, RuCl3 (50 mg) were added to a round bottom flask (100mL) with EG (25 mL) and deionized water (25 mL) under 15 min of ultrasonication and vigorous stirring, and heated at 150 °C with an oil bath for 180 min. After cooling down the solution to room temperature, the product was collected by centrifugation and washed three times with water and ethanol.

#### Characterization

The powder X-ray diffraction (PXRD) patterns were collected with a Rigaku MiniFlex 600 X-ray diffractometer (Cu Kα). The morphology of samples was recorded with a field-emission scanning electron microscope (FE-SEM, Hitachi, SU8010) operated at 5 kV and 10 mA. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images and energy-dispersive X-ray spectroscopy (EDX) data were recorded with a spherical aberration corrected transmission electron microscope (SAC-TEM, JEM-ARM200P) operated at 200 kV. The chemical states of elements were probed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Nexsa). The surface profile and potential were obtained with an atomic force microscope (AFM) and Kelvin probe force microscope (KPFM; Bruker Dimension Fastscan). The precise element composition was detected with an inductively coupled plasma-

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emission spectrometer (ICP-OES) equipped with an Agilent 5110 spectrometer. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were conducted on a Thermo Scientific Nicolet iS20 spectrometer.

The hydrogen spillover effect was investigated by temperature-programmed reduction (TPR) with a chemisorption analyser (BELCAT II, MicrotracBEL). Before TPR test, samples (51 mg) were heated to 100 °C at a ramp rate of 10 °C min<sup>-1</sup>, kept at 100 °C for 30 min to remove adsorbed H<sub>2</sub>O, and cooled to 50 °C under nitrogen atmosphere. Then the samples were kept for 60 min in 10% H<sub>2</sub>–90% N<sub>2</sub> flow at a flow rate of 30 mL min<sup>-1</sup>. Finally, the samples were heated to 900 °C at a ramp rate of 5 °C min<sup>-1</sup> in a 10% H<sub>2</sub>–90% N<sub>2</sub> flow at a flow rate of 30 mL min<sup>-1</sup>.

#### Catalytic CO<sub>2</sub> hydrogenation

The catalytic performances of *m*RTH for CO<sub>2</sub> hydrogenation were evaluated with a commercial evaluation system (CEL-HPR100T+, Beijing China Education Au-Light Co., Ltd). Typically, catalyst powder (40 mg) was placed in a quartz cup (150 mL) that was sealed within stainless steel and transferred into an autoclave. A CO<sub>2</sub>/H<sub>2</sub> mixture (CO<sub>2</sub>:H<sub>2</sub> = 1:4; 4 bar) was filled in the autoclave after evacuation for several times, and allowed to proceed at 200 °C. The products were detected with a gas chromatography (FL 9790) equipped with a flame ionization detector and thermal conductivity detector.

## **Results and discussion**

mRTH were prepared by a wet synthesis procedure, using EG as reductant (cf. Experimental for details). As presented in the typical SEM and TEM images in Fig. 1a and S1, TiH<sub>2</sub> are large particles with size of around 2–10  $\mu$ m, which show a lattice spacing of 2.58 Å corresponding to the (111) lattice plane of cubic TiH<sub>2</sub>.<sup>25, 27-29</sup>. Each microscale TiH<sub>2</sub> particle is coated with Ru NPs of around 3 nm in average diameter, to form mRTH with hybrid structure (Fig. 1b-d). Interesting, the Ru NPs exist in the form of large aggregates of 30-100 nm in diameter (Fig. 1c & Fig. 2a-g), which is likely due to the aggregation of adjacent Ru NPs induced by van der Waals interactions.<sup>30, 31</sup> Each small Ru NP in large Ru aggregates can be identified in HRTEM image (Fig. 1d), which shows a lattice spacing of 2.03 Å corresponding to the (101) plane of Ru with hexagonal crystalline structures.<sup>32</sup> The EDX element maps of mRTH (m = 100 in Fig. 1e; m = 50, 150, and 200 in Fig. 2h-j, respectively) confirm the elemental composition of Ru and Ti in the samples, and the precise content of Ru and Ti is determined by ICP-OES (Table S1), which gives a a Ru loading of 5.7, 9.8, 15.5, and 17.3 wt % in 50-, 100-, 150-, and 200RTH, respectively. The appearance of O in the EDX elemental maps should be attributed to the formation of  $TiO_xH_v$ layer on the surface of TiH<sub>2</sub>, which is induced by the oxidation of TiH<sub>2</sub> by atmospheric oxygen under ambient conditions.<sup>33, 34</sup> The PXRD patterns of mRTH show a set of peaks centred at 34.9, 40.5, 58.6, 70.1, and 73.7°, respectively, which is indexed to cubic TiH<sub>2</sub> (PDF #07-0370). By contrast, the PXRD peaks of hexagonal Ru (PDF #06-0663) located at 44.0° are only visible in the mRTH samples with high Ru loading in 100-, 150-, and





200RTH; the PXRD peaks of Ru in 50RTH samples is almost invisible, likely due to the low loading of Ru NPs with small size (*ca*. 3 nm).<sup>35-38</sup> The PXRD patterns, together with the TEM images and EDX element maps, thus collectively verify the hybrid Ru/TiH<sub>2</sub> structure of *m*RTH.

It is worth noting that the spatial dispersion of Ru NPs in mRTH relates closely to Ru loading (Fig. 2). As the Ru loading increases, Ru NPs organize into discrete aggregates in 50RTH (5.7 wt %), a dense layer of Ru NP aggregates in 100RTH (9.8 wt %), a dense Ru NP aggregate layer with excess Ru aggregates in 150RTH (15.5 wt %), and dense double aggregate layers in 200RTH (17.3 wt %); meanwhile, the size of Ru NP aggregates in 100-, 150- and 200RTH is comparable (ca. 52 nm), while the size of Ru NP aggregates in 50RTH is smaller (ca. 38 nm) due to the low surface coverage of Ru NPs on TiH<sub>2</sub> (cf. Fig. 1b–d and Fig. 2b–g). Moreover, all the Ru NP aggregates are in direct contact with TiH<sub>2</sub> in 50- and 100RTH. In contrast, only the first Ru NP aggregate layer is in direct contact with TiH<sub>2</sub>, while the other Ru NP aggregates are separated by the first Ru layer in 150- and 200RTh. Such differences in the surface coverage, size, and spatial organization of Ru NP aggregates leads to the varied interfacial structure of mRTH, which in turn, as demonstrated later in this work, have critical impact on the MSI (interfacial



Fig. 2 (a) Schematic illustration of spatial dispersion of *m*RTH with increasing Ru loading. (b–d) SEM and (e–g) TEM images, and (h–j) EDX element maps of *m*RTH (*m* = 50, 150, and 200). cf. the data for 100RTH in Fig. 1b–e.

electron transfer and hydrogen spillover) and the consequent catalytic activity of *m*RTH towards CO<sub>2</sub> methanation.

The MSI between Ru NPs and TiH<sub>2</sub> were systematically investigated by AFM coupled with KPFM, XPS, and H<sub>2</sub>-TPR. AFM-KPFM was first used to investigate the charge transfer behaviour in *m*RTH. By selecting single particle of TiH<sub>2</sub> and *m*RTH (Fig. 3a–e), the typical surface potential of TiH<sub>2</sub> and *m*RTH can be obtained and compared by contact potential difference (CPD) given by CPD =  $E_{sample} - E_{substrate}$ , where  $E_{sample}$  and  $E_{substrate}$ are the measured surface potential of sample and substrate, respectively, and *n*–Si(111) was used as the substrate for our **Journal Name** 

KPFM measurements (Fig. 3f-j and Table S2).<sup>39, 40</sup> The CPD shows a positive corelation with the Ru loading in sample, increasing from -8 mV for TiH<sub>2</sub>, to 2 mV for 50RTH, 26 mV for 100RTH, 37.4 mV for 150RTH, and 68.8 mV for 200RTH. The CPD shift from negative (TiH<sub>2</sub>) to positive (*m*RTH) values confirms the electron transfer from TiH<sub>2</sub> to Ru NPs.<sup>41</sup> Moreover, due to the positive correlation between CPD and Fermi level, 50RTH with the lowest positive CPD should have the lowest Fermi level among all *m*RTH, which thus should allow for the easiest electron transfer from TiH<sub>2</sub> to Ru NPs.<sup>40</sup>

To obtain more details about the interfacial electron transfer and the chemical states of interface species in mRTH, XPS spectra were collected. For TiH<sub>2</sub> and *m*RTH, the high-resolution XPS spectra of Ti  $2p_{3/2}$  and Ru  $3d_{5/2}$  indicate that in all samples the surface Ti species exist in the forms of Ti<sup>4+</sup> and defective  $TiO_{2-x}$  in the  $TiO_xH_y$  surface layer (Fig. 4a; cf. Table S3 for the binding energy corresponding to each peak), and Ru exists in the form of Ru<sup>0</sup> and Ru<sup>4+</sup> (Fig. 4b).<sup>27, 28, 33, 34, 42, 43</sup> The formation of TiO<sub>2-x</sub> and Ru<sup>4+</sup> is induced by the spontaneous oxidation of TiH<sub>2</sub> and Ru surfaces by atmospheric oxygen under ambient conditions,<sup>7, 34, 43, 44</sup> which agrees well with the results of EDX element maps shown in Fig. 1e. Moreover, as compared with TiH<sub>2</sub>, the *m*RTH samples show increasing binding energies of Ti<sup>4+</sup> and defective TiO<sub>2-x</sub>, and the binding energy shifts increase steadily from 50RTH to 200RTH. In contrast, the mRTH samples present decreasing binding energies of Ru<sup>0</sup> and Ru<sup>4+</sup> as compared with Ru NPs, and the absolute binding energy shifts decrease steadily from 50RTH to 200RTH (Fig. 4b). Such opposite binding energy shift trends in TiH<sub>2</sub> and Ru NPs imply interfacial electron transfer from  $TiO_xH_y$  to Ru, which agrees well with our KPFM results (Fig. 3) and thus confirms the MSI in mRTH. Notably, the interfacial electron transfer from  $TiO_xH_v$  to Ru results in the formation of electron-enriched Ru species (Ru<sup> $\delta-1$ </sup>) in *m*RTH. As demonstrated later in this work, the Ru species are the dominate sites for CO<sub>2</sub> absorption; moreover, electronenriched Ru species could benefit the chemisorption of CO<sub>2</sub> and the formation of  $[O=C=O]^{\delta-}$  intermediates, and thus efficiently accelerate the CO<sub>2</sub> methanation reaction. It is worth noting that



Fig. 3 (a–e) AFM height images and (f–j) the corresponding KPFM potential profiles of TiH<sub>2</sub> and *m*RTH. (a, f) TiH<sub>2</sub>, (b, g) 50RTH, (c, h) 100RTH, (d, i) 150RTH, and (e, j) 200RTH. CPD in (f–j) is estimated by the potential difference between site A (sample) and B (substrate).

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Fig. 2 (a–c) High-resolution XPS spectra of Ru NPs, TiH<sub>2</sub>, and *m*RTH, (a) Ti  $2p_{3/2}$ , (b) Ru  $3d_{5/2}$ , and (c) O 1s. (d) H<sub>2</sub>-TPR profiles of TiH<sub>2</sub> and *m*RTH.

the interfacial electron transfer from TiO<sub>2</sub> to metal NPs (e.g., Ru,<sup>7</sup> Pt,<sup>25</sup> and Ni<sup>45</sup>) typically occurs in the case of SMSI, which is induced by the partial reduction of TiO<sub>2</sub> support when treated at high-temperature (typically, >300 °C) and under H<sub>2</sub> atmospheres. In contrast, for the TiO2-supported metal NPs (e.g., Ru<sup>20</sup> and Au<sup>46</sup>) prepared under mild conditions that disfavour support reduction, the electron transfer usually occurs in opposite direction, that is, from metal NPs to TiO<sub>2</sub>. Therefore, the unusual charge transfer from  $TiO_xH_y$  to Ru NPs in our mRTH prepared under mild condition (wet synthetic process; see details in Experimental) should be attributed to the highly active, negatively charged  $H^-$  in TiH<sub>2</sub>, which leads to the spontaneous oxidation of  $TiH_2$  surface into  $TiO_xH_y$  layer consisting of oxides and oxyhydrides (cf. Ref. 23 and also the Ti  $2p_{3/2}$  and O 1s XPS spectra in Fig. 4), and thus enables the TiO<sub>x</sub>H<sub>y</sub> surface layer to acts as partially reduced oxide support for Ru NPs, similar to the role of TiO<sub>2</sub> partially reduced at hightemperature and under H<sub>2</sub> atmospheres in the case of SMSI.

To rationalize the opposite impact of Ru loading on the peak shifts in the Ti  $2p_{3/2}$  and Ru  $3d_{5/2}$  XPS spectra of *m*RTH, the spatial dispersion of Ru NPs on TiH<sub>2</sub> has to be taken into account. Note that the XPS spectra are collected based on a typical spot size of  $30-500 \mu$ m, much larger than the size of all *m*RTH samples (< 5  $\mu$ m; cf. Fig. 1–2), the XPS peak position could be regarded as a rough indicator of the binding energy averaged over all the surface Ti or Ru species, in which the surface Ti species could be estimated to be the same for all *m*RTH and the surface Ru species reply specifically on the Ru loading in each *m*RTH. Generally, increasing Ru loading leads to raised surface layer of TiH<sub>2</sub>, and accordingly enhanced overall MSI at the interface. In such a way, the MSI shows increasing impact on the binding energy of the surface Ti species of TiH<sub>2</sub> (approximately the same

for all mRTH), and thus the Ti 2p<sub>3/2</sub> XPS peaks continuously shift upwards as the the Ru loading in 50-, 100-, 150- and 200RTH steadily increases (Fig. 4a). Notably, 100RTH presents much more remarkable shift of the Ti 2p<sub>3/2</sub> XPS peak position than 50RTH, which could be attributed to the much greater surface density of Ru NP aggregates in 100RTH (9.8 wt %; vs. 5.7 wt % in 50RTH). Moreover, the Ru NP aggregates in the second layer of 150- and 200RTH are in indirect contact with the surface layer of TiH<sub>2</sub>, and thus are less efficiently involved in MSI as compared with the Ru NP aggregates in the first layer that are in direct contact with the surface layer of TiH<sub>2</sub>. Although the overall MSI shows a rising trend as the Ru loading in 100-, 150- and 200RTH steadily increases, the overall MSI averaged over all the surface Ru species are declining, thus having a decreasing impact on the binding energies of surface Ru species and leading to downward shifts in the Ru  $3d_{5/2}$  XPS peak position (Fig. 4b). Moreover, in the case of 50- and 100RTH with all the Ru NP aggregates in direct contact with the surface layer of TiH<sub>2</sub>, the notable shift in the Ru 3d<sub>5/2</sub> XPS peak of 50RTH is likely due to the smaller size of Ru NP aggregates in 50RTH (38 nm; vs. 52 nm for 100RTH), which results in much stronger MSI and consequently much greater impact on the binding energies of Ru species in 50RTH.

The O 1s spectra of mRTH and TiH<sub>2</sub> are also analysed. As shown in Fig. 4c, all the O 1s spectra show three types of O species that correspond to the lattice O in TiO<sub>x</sub>H<sub>y</sub> and RuO<sub>2</sub> (denoted as O1), the O at defect (oxygen vacancy) sites or Ti-OH (O2), and the O in chemically adsorbed oxygen-containing species like H<sub>2</sub>O (O3).<sup>25, 33</sup> The appearance of O1 and O2 peaks confirms the partial oxidation of surface TiH<sub>2</sub> resulted from the highly active nature of the negatively charged  $H^-$  in TiH<sub>2</sub>. Moreover, the Ru loading in mRTH correlates with greater integrated peak areas of O2 and O3, which is likely due to the low migration energy of H<sup>-</sup> at the Ru–metal hydride interface.<sup>26</sup> Briefly, the low migration energy favors the migration of H<sup>-</sup> from TiH<sub>2</sub> to the Ru, and higher Ru loading thus allows for the formation of more oxides and oxyhydrides of Ti through ambient oxidation of H<sup>-</sup> at the interface, and gives rise to the increased peak areas of O2. Both the oxygen vacancy and OH group in TiO<sub>x</sub>H<sub>y</sub> surface layer have good binding affinity to H<sub>2</sub>O under ambient conditions,47,48 thus leading to enhanced adsorption of H<sub>2</sub>O and increased peak area of O3 at higher Ru loading level.

H<sub>2</sub>-TPR was also used to further evaluate the Ru–TiH<sub>2</sub> MSI as well as the reducibility of TiH<sub>2</sub> support.<sup>49</sup> As presented in Fig. 4d, all the H<sub>2</sub>-TPR profiles of TiH<sub>2</sub> and *m*RTH show two H<sub>2</sub> consumption peaks in the temperature range of 250–750 °C, one centred in the range of 400–450 °C corresponding to the hydrogen storage by  $\beta$ -TiH<sub>x</sub> phase in TiH<sub>2</sub>, and the other centred at 580 °C corresponding to the hydrogen storage by  $\alpha$ -Ti phase in TiH<sub>2</sub>.<sup>50-53</sup> The later peaks locate at almost the same temperature for TiH<sub>2</sub> and *m*RTH, in agreement with the results reported in literature.<sup>25</sup> In contrast, the former peaks related to the reduction of TiO<sub>x</sub>H<sub>y</sub> surface layer and bulk TiH<sub>2</sub> shift towards lower temperature when the Ru loading in *m*RTH increases, indicating improved reducibility of TiH<sub>2</sub> could be interpreted as a consequence of Ru–TiH<sub>2</sub> MSI. Specifically, as implied by the XPS

spectra in Fig. 4a–c, the charge transfer from TiH<sub>2</sub> to Ru increases the electron density at the Ru–TiH<sub>2</sub> interface, and thus enables the surface TiO<sub>x</sub>H<sub>y</sub> layer to be partially reduced at a lower temperature. Moreover, H<sub>2</sub> could be remarkably activated by TiO<sub>x</sub>H<sub>y</sub>-supported Ru NPs through hydrogen spillover effect<sup>54-56</sup>, and oxygen vacancies on TiO<sub>x</sub>H<sub>y</sub>-support could further enhance the hydrogen spillover effect by facilitating the transfer of active hydrogen species,<sup>57</sup> thus further enhancing the reducibility of TiH<sub>2</sub>. As both the Ti–Ru charge transfer behaviour and the hydrogen spillover effect are positively related to the Ru loading (abundant active hydrogen species can be generated by more Ru NPs), 200RTH with the highest Ru loading shows notable decrease, from 469.7 to 401.1 °C, in the peak temperature for the reduction of TiH<sub>2</sub>.

The catalytic performances of *m*RTH towards  $CO_2$  methanation were evaluated at 200 °C and in an autoclave filled with 4 bar of reaction gas of stoichiometric ratio (20 vol.%  $CO_2$  and 80 vol.% H<sub>2</sub>). Control experiments using TiH<sub>2</sub> support and Ru NPs as catalysts were also conducted under otherwise identical conditions. Approximately, the conversion of  $CO_2$  with representative catalysts (TiH<sub>2</sub>, Ru NPs, and 100RTH; Fig. 5a) increases linearly with reaction time, which shows a typical feature of heterogeneous catalysis occurring on the catalyst surface and implies a reaction kinetics depending primarily on the surface properties of catalysts. An overall comparison of  $CO_2$  conversion and  $CH_4$  selectivity between TiH<sub>2</sub>, Ru NPs, and *m*RTH are presented in Fig. 5b. Despite notable difference in

CO<sub>2</sub> conversion, all the TiH<sub>2</sub>, Ru NPs, and *m*RTH show superior CH<sub>4</sub> selectivity of >99.4%. Moreover, all *m*RTH show remarkably improved conversion (44.7, 86.5, 72.8, and 61.0% for 50-, 100-, 150-, and 200RTH, respectively) as compared with Ru NPs (29.0%) and TiH<sub>2</sub> (1.2%), which thus indicates notable synergistic effect between TiH<sub>2</sub> and Ru. The superior selectivity and activity towards CO<sub>2</sub> methanation demonstrates the advantages of mRTH over traditional Ru–TiO<sub>2</sub> heterogeneous catalyst prepared under similar mild conditions and SMSImediated Ru-TiO<sub>2</sub> heterogeneous catalysts synthesized by high-temperature reduction.<sup>8, 20</sup> As compared with the former one, mRTH show superior selectivity and activity towards CH<sub>4</sub> production, resulting from the usual electron transfer from  $TiO_xH_y$  surface layer to Ru NPs that leads to the generation of electron-enriched Ru NPs with enhanced activation capability for CO intermediates. As compared with the later one, the superior activity of *m*RTH could be attributed to the efficiently exposed Ru NPs, whose activity are otherwise largely impaired due to the coverage of adverse oxide overlayers in SMSImediated Ru–TiO<sub>2</sub> heterogeneous catalysts.

A more accurate comparison of the catalytic activities between TiH<sub>2</sub>, Ru NPs, and *m*RTH was made based on specific activities, which are indicated by the reaction rate of CH<sub>4</sub> with respect to the total catalyst mass (denoted as  $r(CH_4, Cat.)$ ) or the mass of Ru in each catalyst (denoted as  $r(CH_4, Ru)$ ), respectively (Fig. 5c). Given the same mass of catalysts used in CO<sub>2</sub> methanation, the trend in  $r(CH_4, Cat.)$  is, as expected, in line



Fig. 3 Reaction kinetics of catalytic  $CO_2$  methanation and catalyst stability. (a) Typical  $CO_2$  conversion curves as a function of reaction time. (b)  $CO_2$  conversion and  $CH_4$  selectivity after 5 h of reaction. (c) Reaction rate of  $CH_4$ with respect to catalyst mass and Ru mass in catalyst, (d) Catalyst stability of 100RTH.

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with the trend in  $CO_2$  conversion. However,  $r(CH_4, Ru)$  shows two different features: (1) impressively, 50-, 100, 150-, and 200RTH delivers a large r(CH<sub>4</sub>, Ru) of 167.8, 168.7, 81.2 and 54.8 mmol  $h^{-1}$  g<sub>Ru</sub><sup>-1</sup>, which is 21.0, 21.1, 9.6, and 6.2 times higher than that of Ru NPs (7.6 mmol  $h^{-1} g_{Ru}^{-1}$ ), respectively, and thus implies that the catalytic activity of Ru NPs can be remarkably enhanced by TiH<sub>2</sub> support; (2) 50- and 100RTH with low loading of Ru NP aggregates in direct contact with TiH<sub>2</sub> surface show very comparable  $r(CH_4, Ru)$  of 167.8 and 168.7 mmol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup>, respectively, which are both much higher than 150- and 200 RTH with high loading of Ru NP aggregates in both direct and indirect contact with TiH<sub>2</sub> surface. The two features of r(CH<sub>4</sub>, Ru) clearly indicate that the Ru-TiH<sub>2</sub> interface could substantially increase the catalytic activity of Ru, and direct Ru-TiH<sub>2</sub> contact induces much more efficient interface for boosting the catalytic activity of Ru than indirect Ru-TiH<sub>2</sub> contact. These results thus confirm and highlight the critical role of appropriate Ru-TiH<sub>2</sub> MSI on the catalytic activity of mRTH towards CO<sub>2</sub> methanation, which will be discussed in detail later in this work. Moreover, despite comparable specific activity of Ru NPs in 100RTH and 50RTH, 100RTH is selected as the optimum catalyst for CO<sub>2</sub> methanation, due to its higher Ru loading that benefits more efficient utilization of TiH<sub>2</sub> (indicated by higher r(CH<sub>4</sub>, Cat.)). It is also worth noting that catalytic activity of 100RTH, indicated by its  $r(CH_4, Ru)$  up to 168.7 mmol h<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup>, is superior to most of the Ru-based heterogeneous catalysts reported in literature, and thus enables 100RTH to be among the best Ru-based heterogeneous catalysts for CO<sub>2</sub> methanation, particular those working efficiently at temperature ≤200 °C (cf. Table S4).

The stability of mRTH was also evaluated. Taking 100RTH for instance, the CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity show

neglectable change even after 5 cycles (equivalently, 25 h; Fig. 5d) of successive operation, which thus demonstrates its excellent cycling stability.

To get insights into the excellent catalytic activity of 100RTH and the activity differences between various mRTH, two important control experiments were adequately designed and conducted, and TiH<sub>2</sub>, Ru, and 100RTH were selected as representative catalysts. The first one was the sorption of CO<sub>2</sub> on catalyst surfaces, in which CO2 was first allowed to be adsorbed on catalyst surface at 30 °C for 30 min, and then desorbed at elevated temperature (5 °C min<sup>-1</sup>) in N<sub>2</sub> flow (50 mL min<sup>-1</sup>). The whole sorption processes were monitored with in situ DRIFTS. As shown in Fig. 6a-c, the DRIFTS spectra of TiH<sub>2</sub>, Ru, and 100RTH all show absorption peaks at 1640 cm<sup>-1</sup>, which is attributed to the adsorbed  $CO_2$  species of  $[O=C=O]^{\delta-}$  on catalyst surface.<sup>60-62</sup> However, the sorption peaks at 1640 cm<sup>-1</sup> in the spectra of Ru NPs and 100RTH are much more intense than the corresponding peaks of TiH<sub>2</sub> at the same temperature. Moreover, another sorption peaks can also be found at ca. 2100 cm<sup>-1</sup> in the enlarged DRIFTS spectra of Ru NPs and 100RTH, which correspond to  $Ru(CO)_n$  species generated by the partial dissociation of adsorbed CO<sub>2</sub> on Ru NP surfaces.<sup>7, 63, 64</sup> The peaks of  $Ru(CO)_n$  species, however, are not found in the spectra of TiH<sub>2</sub>. Such different sorption behaviour between TiH<sub>2</sub>, Ru, and 100RTH revealed by DRIFTS spectra thus indicates that Ru NPs have much stronger CO<sub>2</sub> adsorption affinity than TiH<sub>2</sub>, and the Ru NPs in 100RTH are the predominant sites for CO<sub>2</sub> adsorption. Moreover, it is of particular interesting to note that Ru NPs and 100RTH show significantly different development trend of the  $Ru(CO)_n$  peaks at elevated temperature. As the temperature increases from 30 to 200 °C, the  $Ru(CO)_n$  peaks of Ru NPs



Fig. 4 (a–c) In situ DRIFTS spectra of  $CO_2$  sorption on (a) Ru NPs, (b) TiH<sub>2</sub>, and (c) 100RTH at varied temperature. (d) Reaction rate of catalytic  $CO_2$  methanation in the absence of external H<sub>2</sub>.

roughly remain their intensity; in sharp contrast, the Ru(CO)<sub>n</sub> peaks of 100RTH decline rapidly in their intensity and even vanishes after keeping 100RTH at 200 °C for 50 min. As revealed below, hydrogen stored in TiH<sub>2</sub> can be released at elevated temperature (Fig. 6d). The rapid declined peak intensity of Ru(CO)<sub>n</sub> in 100RTH thus should be attributed to the reduction of adsorbed CO species by hydrogen released from TiH<sub>2</sub>.<sup>7</sup>

The second control experiment is the CO<sub>2</sub> methanation in the absence of external  $\mathsf{H}_2$  source and under otherwise identical conditions. As expected, despite the high intrinsic activity of RU NPs towards catalytic CO<sub>2</sub> hydrogenation,<sup>65</sup> no product is detected for Ru NPs due to absence of hydrogen (Fig. 6d). In contrast, TiH<sub>2</sub> shows a high H<sub>2</sub> production rate of 298.1 µmol h<sup>-</sup>  $^{1}$  g<sub>cat.</sub><sup>-1</sup>, which is due to the release of hydrogen stored in TiH<sub>2</sub> and thus verifies the hydrogen storage and release capability of  $TiH_2$ .<sup>28, 51</sup> This explains why  $CO_2$  can be reduced by  $TiH_2$  even in the absence of external  $H_2$  source. However, the negligible production rate of CH<sub>4</sub> and low selectivity of CH<sub>4</sub> over CO (denoted by the CH<sub>4</sub>/CO rate ratio) indicate the poor intrinsic activity of TiH<sub>2</sub> towards catalytic CO<sub>2</sub> methanation. As compared with TiH<sub>2</sub>, 100RTH delivers 22 times higher CH<sub>4</sub> production rate and 1.9 times higher CH<sub>4</sub> selectivity. These results, together with the results shown in Fig. 6a-c, collectively suggest that the Ru NPs in 100RTH are not only the predominant sites for CO<sub>2</sub> adsorption but also the predominant catalytic sites for CO2 methanation. We further note that the CH4 selectivity of 100RTH in the absence of  $\mathsf{H}_2$  is much worse than that in presence of stoichiometric amount of H<sub>2</sub> (Fig. 6a), which should be to the limited amount and very low partial pressure of H<sub>2</sub> released from TiH<sub>2</sub>.66

Based on all the above discussion, we propose a plausible relationship between structure, MSI and catalytic performance of *m*RTH (Scheme 1). As well demonstrated in literature, the activation of carbonyl and hydrogen plays a critical role in efficient  $CO_2$  methanation.<sup>7, 8, 16</sup> The carbonyl with partially positively charged C atoms in  $CO_2$  and  $Ru(CO)_n$  intermediates can be activated by directing electron transfer from support to Ru NPs, which is beneficial for carbonyl to get electrons from electron-enriched Ru NPs and thus to be easily stabilized for subsequent conversion into CH<sub>4</sub>. Moreover, although hydrogen



Scheme 1. Proposed relationship between structure, MSI and catalytic performances of mRTH towards CO<sub>2</sub> methanation.

activation can be readily achieved on Ru NPs through spillover effect, excess Ru NPs should be avoided, since intense hydrogen spillover effect can be induced, which inversely leads to deteriorative catalytic activity towards CO<sub>2</sub> methanation by strengthening the adsorption of H<sub>2</sub>O molecules and hindering the removal of H<sub>2</sub>O molecules from catalyst surfaces.<sup>16</sup> Accordingly, the interfacial charge transfer and Hydrogen spillover effect should be well regulated for optimal catalytic activity. In our *m*RTH, benefitting from the TiO<sub>x</sub>H<sub>y</sub> surface layer on TiH<sub>2</sub> and the direct Ru–TiO<sub>x</sub>H<sub>y</sub> contact in 50- and 100RTH, notable electron transfer from Ti to Ru can be achieved under mild synthetic condition (Fig. 4), which enriches the electron on Ru NPs and thus facilitate the carbonyl activation for efficient CO<sub>2</sub> methanation. Meanwhile, the low to moderate Ru loading in 50- and 100RTH allows favourable hydrogen spillover effect (positively corelated to the Ru loading) for efficient CO2 methanation by hydrogen activation. Therefore, the electron transfer and hydrogen spillover effect in 50- and 100RTH collectively contribute to the superior catalytic activity towards efficient CO<sub>2</sub> methanation. By comparison, the higher loading Ru NPs with partially indirect  $Ru-TiO_xH_y$  contact in 150- and 200RTH induces less sufficient Ti-Ru electron transfer for carbonyl activation, and disadvantageous hydrogen spillover effect due to the enhanced adsorption of H<sub>2</sub>O molecules on catalyst surface, which in turn results in their much lower activity towards CO<sub>2</sub> methanation.

#### Conclusions

In conclusion, we have developed a new heterogeneous catalyst of TiH<sub>2</sub>-supported Ru NPs for highly efficient CO<sub>2</sub> methanation. Benefitting from the highly active, negatively charged hydrogen species of  $H^-$  in TiH<sub>2</sub>, the TiH<sub>2</sub>-supported Ru NPs show usual charge transfer from support to Ru NPs, which has not been achieved in the traditional TiO2-supported Ru catalysts synthesized under similar mild conditions. Instead, TiH<sub>2</sub>supported Ru NPs show charge transfer behaviour similar to that in SMSI-mediated TiO2-Ru catalysts prepared under high temperature reduction conditions. Moreover, as compared with SMSI-mediated TiO<sub>2</sub>-Ru catalysts, the far milder synthetic condition for TiH<sub>2</sub>-supported Ru NPs avoids the formation of adverse oxide overlayer on Ru NPs, which leads to the remarkably enhanced activation of CO intermediates on the TiH<sub>2</sub>-supported, electron-enriched and efficiently exposed Ru NPs. Meanwhile, H<sub>2</sub> can also be activated by TiH<sub>2</sub>-supported Ru NPs via hydrogen spillover effect, inevitably accompanied by the adverse hydration of catalyst surface. The electron transfer behaviour and hydrogen spillover effect are readily regulated by tuning the Ru loading, and a moderate Ru loading of 9.8 wt.% in 100RTH is optimized, in which the impacts of Ru loading on CO intermediate activation, H<sub>2</sub> activation and catalyst surface hydration are synergistically balanced. When evaluated at a low reaction temperature of 200 °C and under 4 bar pressure, 100RTH is capable of delivering a notable CH<sub>4</sub> selectivity of 99.8% and a remarkable CH<sub>4</sub> production rate of 168.7 mmol  $h^{-1}$  g<sub>Ru</sub><sup>-1</sup>, which is 21.1 times more active than pure Ru NPs. Our work thus opens up a new avenue for the development of advanced

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heterogeneous catalysts for the efficient conversion of CO<sub>2</sub> into value-added chemicals.

# **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

# **Conflicts of interest**

There are no conflicts to declare.

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# Table of Contents (ToC)

TiH<sub>2</sub>-support Ru catalyst is developed for highly efficient CO<sub>2</sub> methanation, in which usual support-to-metal electron transfer behaviour and hydrogen spillover effect are synergistically regulated to balance CO intermediate activation, H<sub>2</sub> activation and catalyst surface hydration.

# **ToC Figure**

