## **Green Chemistry**



**PAPER** 

View Article Online
View Journal | View Issue



**Cite this:** *Green Chem.*, 2020, **22**, 6855

# Tuning selectivity of CO<sub>2</sub> hydrogenation by modulating the strong metal-support interaction over Ir/TiO<sub>2</sub> catalysts†

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Exploration of highly selective catalysts for  $CO_2$  hydrogenation remains a great challenge since the reduction of  $CO_2$  over the supported metal catalysts may give rise to various products in response to the modulation of the chemical state of active sites. Herein, by varying the pretreatment temperature of iridium/titanium oxide ( $Ir/TiO_2$ ) catalysts, the selectivity of  $CO_2$  hydrogenation from  $CH_4$  to sole production of CO can be finely tuned. The change of product selectivity is achieved in such a way that the selectivity greatly depend on the formation of a reduced  $TiO_x$  overlayer around Ir nanoparticles (IRSI) as originated from the strong metal–support interaction (IRSI). With only a weak reduction treatment, the exposed Ir IRSI without a IRSI coating promote IRSI production exclusively. After the catalyst undergoes a high temperature reduction, the evolution of the IRSI coating over Ir IRSI shows a preference for IRSI production with an inhibition of further methanation. This study not only provides insights into the regulation of IRSI hydrogenation by IRSI but also serves as an effective approach to tuning other catalytic processes

Received 6th July 2020, Accepted 15th September 2020 DOI: 10.1039/d0gc02302g

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#### Introduction

The ever-increasing threats of global warming and dramatic climate changes have drawn increasing attention in recent years. Carbon dioxide ( $CO_2$ ), as a major greenhouse gas, is being blamed for the ecological troubles. On the other hand,  $CO_2$  also serves as an ideal C1 source, and catalytic  $CO_2$  hydrogenation offers an effective strategy for the transformation of  $CO_2$  into high value-added chemicals<sup>1–3</sup> and fuels<sup>4–6</sup> by which the global carbon cycle can be sustained simultaneously.

Catalytic  $CO_2$  hydrogenation at atmospheric pressure usually consists of two competitive processes over the supported Group VIII metal catalysts. One is direct  $CO_2$  methanation, known as the Sabatier reaction,  $^{7-9}$  and the other is  $CO_2$  hydrogenation to carbon monoxide (CO), known as the reverse

water-gas shift (RWGS) reaction. 10-12 Exploration of highly

Reducible oxides like titanium oxide  $(TiO_2)$  and cerium oxide  $(CeO_2)$  are widely used as supports in  $CO_2$  hydrogenation, as they give adequate assistance for  $CO_2$  activation. <sup>23–25</sup> More importantly, strong metal–support interactions (SMSI)

selective catalysts with the aim of acquiring desired products for each process still remains a great challenge. So far, enormous efforts have been devoted to tuning the selectivity of CO<sub>2</sub> hydrogenation, including tuning the metal particle size, 13-15 modifying the chemical state, changing the support type<sup>16,17</sup> or crystal phase, 18 and adding promoters. 17,19 Despite these developments, intrinsic factors that govern the product selectivity remain less understood. As previously reported by Christopher et al., the product selectivity of CO<sub>2</sub> hydrogenation greatly depended on the active sites, that is, atomically dispersed isolated rhodium (Rh) sites selected for CO production and Rh nanoparticles (NPs) selected for CO<sub>2</sub> methanation.<sup>20</sup> Our group has reported recently that, when decreasing the coordination number of metal sites to one, CO production was significantly enhanced by the inhibition of carbonyl dissociation and simultaneous facilitation of CO desorption.<sup>21</sup> On the other hand, researchers have found that it was the chemical state of Ir species, rather than the coordination of metals, nanoparticles or single-atoms, that played a more important role in controlling product selectivity.<sup>22</sup>

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<sup>†</sup>Electronic supplementary information (ESI) available: Additional characterizations of Ir/TiO<sub>2</sub> catalysts. See DOI: 10.1039/d0gc02302g

Paper Green Chemistry

on reducible oxide-supported metal catalysts occur, 26-28 where H<sub>2</sub> and CO chemisorption can be suppressed and will further influence the catalytic CO2 hydrogenation processes. The intrinsic role of SMSI in tuning the selectivity of CO2 hydrogenation is worth studying in depth.

In this study, we succeeded in fabricating a highly dispersed Ir/TiO2 catalyst with resistance to agglomeration even when treated at high temperatures (up to 700 °C). By varying the reduction temperature, SMSI on Ir/TiO2 are modulated, which further plays a crucial role in tuning the product selectivity. With a weak reduction treatment at low temperatures (lower than 300 °C), metallic Ir NPs expose on the catalyst surface and promote CH<sub>4</sub> production exclusively. After the catalyst undergoes a high temperature reduction, Ir NPs are entirely encapsulated by reduced TiOx species, which show a preference for CO production with an inhibition of further methanation. With this knowledge, we show that highly selective CO2 hydrogenation processes toward either of the two products can be achieved by tailoring the SMSI over the supported metal catalysts.

#### Results and discussion

#### Catalytic performance of Ir/TiO<sub>2</sub>-x catalysts

A series of Ir/TiO<sub>2</sub> catalysts, with a 2.45 wt% Ir loading as detected by inductively coupled plasma optical emission spectroscopy (ICP-OES), were pretreated at different temperatures and were denoted as  $Ir/TiO_2$ -x, where x refers to the reduction temperature (x = 200-700 °C). The catalytic CO<sub>2</sub> hydrogenation tests of these catalysts were performed at 280 °C under atmospheric pressure. As shown in Fig. 1, the series of Ir/TiO<sub>2</sub>-x catalysts show a similar catalytic activity as reflected by the reaction rate, whereas a divergence in product selectivity from CH<sub>4</sub> to CO is observed with an increase in the reduction temperature from 200 to 700 °C. Samples pretreated at temperatures lower than 300 °C exhibited complete methanation of CO2 conversion. An improved selectivity toward CO was observed as the reduction temperature increased, and a further increase of reduction temperature beyond 600 °C led to complete CO formation.

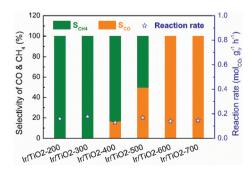


Fig. 1 Catalytic performance of the series of Ir/TiO<sub>2</sub>-x catalysts for CO<sub>2</sub> hydrogenation reactions. Reaction conditions: 280 °C, 0.1 MPa, space velocity = 9000 mL  $h^{-1}$   $g_{cat}^{-1}$ , and  $H_2/CO_2/N_2 = 70/20/10$ .

The catalytic performance of CO<sub>2</sub> hydrogenation over the Ir/ TiO<sub>2</sub>-x catalysts was then compared with that of state-of-the-art catalysts. As shown in Table S1,† for the CO2 methanation reaction, the activity of the Ir/TiO2-200 catalyst is inferior to that of Ru- and the benchmark Ni-based catalysts since they always exhibit excellent hydrogenation properties. As for the reverse water-gas shift reaction, Ir/TiO2-700 exhibits an activity comparable to or higher than that of the reported catalysts. Nevertheless, the product selectivity on the Ir/TiO<sub>2</sub> catalysts can be tuned from CH4 to exclusively CO just by varying the reduction temperature (Fig. 1 and Fig. S1†), which may help uncover the intrinsic factors that govern product selectivity and may offer greener pathways for the conversion of CO2.

In Fig. 2a, similar slopes of Arrhenius plots for CO<sub>2</sub> conversion are observed, *i.e.*, similar apparent activation energies  $(E_a)$ were calculated for CO<sub>2</sub> activation over these Ir/TiO<sub>2</sub>-x catalysts. However, the slopes of Arrhenius plots for CH<sub>4</sub> production greatly increased along with the increase of pretreatment temperature from 200 to 700 °C (Fig. 2b). A reverse trend is observed for the variation of  $E_a$  for CO production (Fig. S2†). From the calculated data, the  $E_a$  values for  $CH_4$  production manifest a significant increase from 39.6 to 233.9 kJ mol<sup>-1</sup>, while those for CO production appear to exhibit a modest decrease from 50.7 to 41.1 kJ  $\text{mol}^{-1}$  (Table S2†). Note that the  $E_a$  values for  $CO_2$  conversion all lie in a lower value range  $(40.5-47.1 \text{ kJ mol}^{-1})$ , indicative of the facile activation of  $CO_2$ over all Ir/TiO2-x catalysts. The increased barrier for CH4 production together with the decreased barrier for CO production offers a great opportunity for modulating the selectivity in the CO<sub>2</sub> hydrogenation process. The tremendous shift of product selectivity together with the corresponding soaring increase of E<sub>a</sub> for CH<sub>4</sub> production greatly motivates us to investigate the intrinsic variation of Ir/TiO2-x catalysts as the pretreatment temperature varies.

#### Structure identification of Ir/TiO<sub>2</sub>-x catalysts

The structure variations with the increasing pretreatment temperature of Ir/TiO2 catalysts were first studied by a set of characterization techniques. As shown in Fig. S3 and Table S3,† these Ir/TiO<sub>2</sub>-x catalysts possess similar BET surface areas and pore volumes. From XRD patterns, there is no characteristic peak for metallic Ir or IrO2 phases for all Ir/TiO2x catalysts (Fig. S4 $\dagger$ ), indicative of a high dispersion of Ir

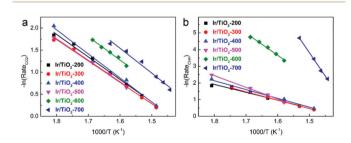


Fig. 2 Arrhenius plots for (a) CO<sub>2</sub> conversion and (b) CH<sub>4</sub> production over  $Ir/TiO_2$ -x catalysts.

**Green Chemistry** Paper

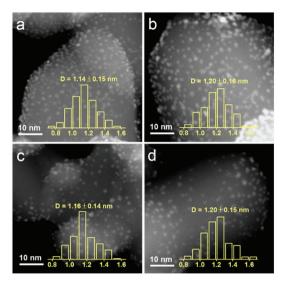


Fig. 3 HAADF-STEM images of the series Ir/TiO2-x catalysts with the metal size distribution. (a) Ir/TiO<sub>2</sub>-200; (b) Ir/TiO<sub>2</sub>-400; (c) Ir/TiO<sub>2</sub>-600; and (d) Ir/TiO2-700.

species on the rutile TiO2 support. As observed from the HAADF-STEM images in Fig. 3, Ir nanoparticles in all these Ir/ TiO<sub>2</sub>-x catalysts are highly dispersed and manifest a uniform size distribution with a diameter of 1.1-1.2 nm. The good stability of Ir NPs was primarily due to the employment of rutile TiO2, which possesses similar lattice parameters with those of rutile IrO2 (Table S4†). Upon calcination in air, IrO2 tends to spread onto TiO2 and facilely forms an IrxTi1-xO2 interphase between surface IrO2 and the TiO2 substrate (IrO2/ Ir<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub>/TiO<sub>2</sub>), which in turn resists the aggregation of Ir NPs even after a pretreatment at a temperature of 700 °C.

The reduction behavior of the as-prepared Ir/TiO<sub>2</sub> catalyst was then acquired by a H2-TPR experiment. As shown in Fig. 4, two main reduction peaks (at 83 and 184 °C) are observed before 300 °C, which are attributed to the reduction of surface  $IrO_2$  and Ir species in the  $Ir_xTi_{1-x}O_2$  interphase, respectively. The H<sub>2</sub> consumption for the two stages (between 50-285 °C) was measured as 253.7 μmol g<sup>-1</sup>, which is approximately equi-

valent to the theoretical estimation of 254.9 µmol g<sup>-1</sup> for IrO<sub>2</sub> reduction (Table S5†). The total H<sub>2</sub> consumption is 1.58 times that of theoretical estimation for full reduction of the IrO2 phase, indicative of the co-reduction of TiO<sub>2</sub> in the Ir/TiO<sub>2</sub> catalyst, which can be confirmed by the broad peaks at 320 and 530 °C. Benefiting from the formation of the Ir<sub>r</sub>Ti<sub>1-r</sub>O<sub>2</sub> interphase, the reduction of TiO2 in Ir/TiO2 is greatly facilitated<sup>29</sup> in comparison with that of pure TiO<sub>2</sub> (at 671 °C) due to the facile hydrogen spillover. Therefore, for the Ir/TiO2 catalysts pretreated at temperatures less than 300 °C, i.e., the Ir/ TiO<sub>2</sub>-200 and Ir/TiO<sub>2</sub>-300 samples, there are predominantly exposed metallic Ir NPs on the surface of TiO<sub>2</sub> support. For the Ir/TiO2 catalysts pretreated at temperatures higher than 300 °C, apart from the reduction of IrO2, there is also coreduction of TiO2. Accordingly, the degree of reduction of Ir/ TiO<sub>2</sub> was supposed to be improved with the increase of pretreatment temperature.

As reported previously, the chemical state of Ir species plays a vital role in tuning the selectivity of CO<sub>2</sub> hydrogenation, that is, metallic Ir NPs preferred CH<sub>4</sub> production while partially oxidized Ir species favored CO production.<sup>22</sup> In our case, the chemical states of Ir/TiO2-x catalysts were then investigated with X-ray photoelectron spectroscopy (XPS). As shown in Fig. 5a, the peaks approximately at 60.5 eV (Ir  $4f_{7/2}$ ) and 63.3 eV (Ir  $4f_{5/2}$ ) are attributed to metallic Ir species.<sup>30,31</sup> In the Ir/  $TiO_2$ -200 sample, both metallic  $Ir^0$  and partially oxidized  $Ir^{\delta+}$ species contribute to the observed binding energies of 61.4 eV (Ir  $4f_{7/2}$ ) and 64.0 eV (Ir  $4f_{5/2}$ ), which is due to the incomplete reduction of Ir NPs as confirmed by H2-TPR results. The shift in binding energy from 61.4 to 60.2 eV with the increase of reduction temperature suggests a gradual improvement of the degree of reduction of Ir NPs. Combined with the reaction data above, the improved degree of reduction failed to promote CH<sub>4</sub> production, indicating that the chemical state of Ir species may not be the decisive factor on product selectivity. It thus motivates us to focus on other discrepancies originating from the variation of micro-structures in Ir/TiO2 influenced by different reduction treatments.

As previously reported by Tauster et al., 26-28 there are strong metal-support interactions (SMSI) over TiO2 supported Ir cata-

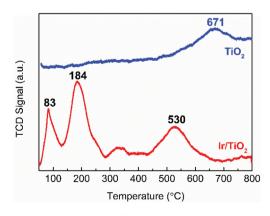


Fig. 4 H<sub>2</sub>-TPR profiles of the Ir/TiO<sub>2</sub> catalyst and the TiO<sub>2</sub> support.

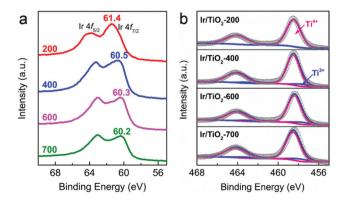


Fig. 5 (a) Ir 4f and (b) Ti 2p XP spectra of Ir/TiO<sub>2</sub>-x catalysts.

Paper Green Chemistry

lysts, in which reduced  $\mathrm{TiO}_x$  species migrates onto the metal surfaces and further forms a coating on the metal particles. Consequently, the chemisorption of CO and  $\mathrm{H_2}$  can be severely suppressed, which usually alters the catalytic performance of  $\mathrm{CO_2}$  hydrogenation. As indicated by the Ti 2p XP spectra (Fig. 5b and Table S6†), the increased  $\mathrm{Ti^{3^+}}$  concentration (from 1.1% to 9.7%) might be a reflection of the enhanced  $\mathrm{TiO}_x$  coating over Ir NPs when the pretreatment temperature was varied from 200 to 700 °C.

HRTEM observations provide intuitive information about the discrepancies in micro-structures with varying reduction temperature. As shown in Fig. 6, the Ir/TiO<sub>2</sub>-200 sample shows angular particles on the TiO2 support with a clear boundary due to a dominant reduction of IrO2 to metallic Ir, while an increased coating over Ir NPs is distinguishable with the prereduction temperature varying from 400 to 700 °C. This phenomenon is ascribed to a gradual migration of TiO<sub>x</sub> overlayer to the Ir NPs. Furthermore, CO was used as a probe in detecting the in situ diffuse reflectance infrared Fourier transform (DRIFT) spectra, with the aim of getting a qualitative comparison of the degree of exposure of Ir NPs after coating by  $TiO_x$  overlayer. The main band appeared at 2080–2040 cm<sup>-1</sup> in the carbonyl region (Fig. 7), which was attributed to the linear CO adsorption on Ir NPs.32 An obvious decay of the DRIFT intensity was observed as the pretreatment temperature varied from 300 to 700 °C, indicative of a reduced Ir exposure, which in turn demonstrated the growth of TiOx coating on Ir NPs. The intensity of CO adsorption on the Ir/TiO<sub>2</sub>-200 sample was found to be a little less than that of Ir/TiO2-300 probably due to the lower degree of reduction of Ir species in Ir/TiO<sub>2</sub>-200.

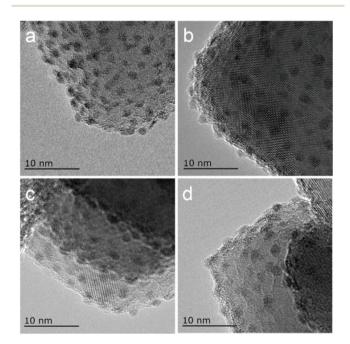


Fig. 6 HRTEM images of the series of  $Ir/TiO_2$ -x catalysts. (a)  $Ir/TiO_2$ -200; (b)  $Ir/TiO_2$ -400; (c)  $Ir/TiO_2$ -600; and (d)  $Ir/TiO_2$ -700.

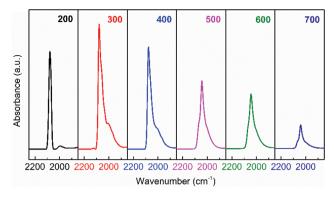


Fig. 7 In situ DRIFT spectra obtained after CO adsorption and evacuation with helium at room temperature (25 °C), over the series of  $Ir/TiO_2-x$  catalysts.

H<sub>2</sub> and CO chemisorption experiments were further conducted to estimate the dispersion of Ir species on  $Ir/TiO_2-x$  catalysts. As shown in Table 1, the values determined by both H<sub>2</sub> and CO probe molecules indicate the same tendency for different Ir/TiO2-x samples, that is, the dispersion of Ir decreases with the increase of reduction temperature from 300 to 700 °C. Ir/TiO<sub>2</sub> catalysts pretreated at temperatures higher than 600 °C even lost their H<sub>2</sub> or CO adsorption ability, which suggests an almost complete encapsulation of Ir NPs by the TiO<sub>x</sub> overlayer. Meanwhile, both H<sub>2</sub> and CO uptakes on the Ir/ TiO<sub>2</sub>-200 catalyst were found to be less than those on Ir/TiO<sub>2</sub>-300, primarily due to the insufficient reduction of Ir/TiO<sub>2</sub>-200, as indicated by H2-TPR and XPS results. The variation in Ir dispersion conforms with the results of HRTEM observations and DRIFT spectra and might be the most likely reason for the selectivity change in CO<sub>2</sub> hydrogenation as all these Ir/TiO<sub>2</sub>-x catalysts manifest an analogous size distribution.

# Structure evolution and the proposed catalytic mechanism of $Ir/TiO_2$ -x catalysts

On the basis of the above observations, a structure evolution of Ir/TiO<sub>2</sub> catalysts at different reduction stages is then proposed (Fig. 8). Benefiting from the similar lattice parameters between IrO<sub>2</sub> and rutile TiO<sub>2</sub>, highly dispersed Ir/TiO<sub>2</sub> catalysts with a desired sintering resistance and similar particle size can be facilely fabricated. By varying the reduction temperature, the strong metal–support interaction in Ir/TiO<sub>2</sub>-x can be modu-

Table 1  $\,$  H<sub>2</sub> and CO chemisorption results for the series of  $\,$  Ir/TiO<sub>2</sub>-x catalysts

Sample	$H_2$ uptake $(\mu mol \ g_{Ir}^{-1})$	D <sub>Ir</sub> by H <sub>2</sub>	CO uptake (µmol g <sub>Ir</sub> <sup>-1</sup> )	D <sub>Ir</sub> by CO
Ir/TiO <sub>2</sub> -200	33.6	52.8%	63.8	50.1%
Ir/TiO <sub>2</sub> -300	36.4	57.2%	69.4	54.5%
Ir/TiO <sub>2</sub> -400	24.0	37.7%	50.2	39.4%
Ir/TiO <sub>2</sub> -500	3.59	5.63%	6.94	5.45%
Ir/TiO <sub>2</sub> -600	2.18	3.42%	4.39	3.44%
Ir/TiO <sub>2</sub> -700	0.12	0.20%	0.29	0.22%

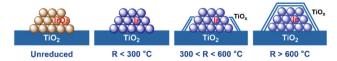


Fig. 8 A schematic illustration of the structural evolution of Ir/TiO<sub>2</sub>-x catalysts. The gradually brighter color on Ir species suggests an improvement of the degree of reduction for Ir NPs.

lated accordingly, where a TiO<sub>x</sub> overlayer gradually appears and migrates on to Ir NPs, resulting in a shrinkage of the metallic Ir surface. The formation of TiO<sub>x</sub> coating by SMSI plays an important role in the selectivity change. For the Ir/  $TiO_2$ -x catalysts treated at lower temperatures (x < 300 °C), there are dominant metallic Ir NPs, on which CO2 methanation can be facilitated as reported in our previous study.<sup>21</sup> As for the samples treated with a moderate reduction (300 < x <600 °C), the TiO<sub>x</sub> overlayer begins to migrate and coat the Ir surface and results in a shrinkage of the metallic Ir surface. In combination with the partially exposed Ir surfaces and a TiO<sub>x</sub> thin layer, both CO<sub>2</sub> methanation and reverse water-gas shift (RWGS) processes will happen on the  $Ir/TiO_2$ -x catalysts. With the increase of TiO<sub>x</sub> coating, the RWGS process producing CO is promoted accordingly. On the contrary, for the samples treated with an excessive reduction (x > 600 °C), Ir NPs are entirely encapsulated with the TiO<sub>x</sub> overlayer. The RWGS process on TiO<sub>x</sub> coating is facile to realize, while further hydrogenation to produce CH4 is completely suppressed due to the unreachable Ir surfaces.

Considering the structural evolution in relation to the corresponding catalytic performance, CO probably serves as the intermediate during  $\rm CO_2$  methanation over  $\rm Ir/TiO_2$ -x catalysts. As all these  $\rm Ir/TiO_2$ -x catalysts manifest similar reaction rates and  $E_a$  for  $\rm CO_2$  conversion with a low value of  $\sim$ 45 kJ  $\rm mol^{-1}$ , it is facile to realize  $\rm CO_2$  activation. An increased barrier for  $\rm CH_4$  production is observed as the reduction temperature increases, during which the encapsulation of Ir NPs results in an enhanced RWGS process to produce CO. When the reduction temperature is increased to modulate the metal-support interaction, the  $\rm TiO_x$  thin layer gradually migrates on to the surface of Ir NPs, which plays a vital role in further transformation of product selectivity from  $\rm CH_4$  to CO.

## Experimental

#### **Catalyst preparation**

Ir/TiO $_2$  catalysts were prepared via a wetness impregnation method. In a typical synthesis, 0.42 g of the  $\rm H_2IrCl_6$  solution (38 wt%, 0.1418 g Ir per gram of solution, AR) was diluted to 50 mL with deionized water. Following this, 2.0 g of rutile  $\rm TiO_2$  was added to the solution and the resulting suspension was dried in a 50 °C water bath with vigorous stirring through evaporation. The resulting solid was dried at 120 °C for 12 h, followed by calcination in air at 400 °C for 4 h. In order to remove the residual chlorides, the sample was then washed

repeatedly with a dilute ammonia solution (1 mol  $L^{-1}$ ), followed by filtration and drying at 80 °C overnight. The sample thus obtained was denoted as the fresh  $Ir/TiO_2$  catalyst. The loading of Ir on the  $Ir/TiO_2$  catalyst was 2.45 wt% as detected by ICP. Prior to  $CO_2$  hydrogenation tests, the as-prepared  $Ir/TiO_2$  sample was reduced *in situ* in a  $H_2$  flow (20 mL min<sup>-1</sup>) at specific temperatures, denoting them as  $Ir/TiO_2$ -x, where x indicates the reduction temperature (200, 300, 400, 500, 600 or 700 °C).

#### Catalyst characterization

Powder X-ray diffraction (XRD) data were acquired using a PANalytical X'Pert-Pro X-ray diffractometer operated at 40 kV and 40 mA. Nitrogen physisorption was performed with a Micromeritics ASAP 2460 instrument at –196 °C. TEM observations, including high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and high-resolution transmission electron microscopy (HRTEM) images, were acquired using a JEOL JEM-2100F microscope operated at 200 kV. The Ir concentration in the Ir/TiO<sub>2</sub> catalyst was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an ICP-OES 7300DV instrument.

 $\rm H_2$  temperature programmed reduction ( $\rm H_2\text{-}TPR$ ) was performed with a Micromeritics AutoChem II 2920 apparatus. Prior to TPR measurement, the pristine  $\rm Ir/TiO_2$  sample was pretreated with Ar at 200 °C for 60 min. After the temperature was reduced to 50 °C, a 10%  $\rm H_2/Ar$  flow was introduced into the reactor by heating the sample to 800 °C at a heating rate of 10 °C min<sup>-1</sup>. The signal was recorded online with a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo Fisher ESCALAB 250Xi instrument, employing monochromated Al K $\alpha$  radiation (hv=1486.6 eV) as the X-ray source. The sample was pretreated at the desired temperature in a  $H_2$  flow and then held under an inert atmosphere, followed by rapid transfer to the sample chamber to minimize exposure to air. The results were calibrated by setting the C 1s adventitious carbon peak position to 284.6 eV.

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectra were acquired using a Bruker Equinox 55 spectrometer recorded with a resolution of 4 cm<sup>-1</sup>. The sample was treated in situ under a H<sub>2</sub> flow (20 mL min<sup>-1</sup>) at the desired temperature for 60 min. After cooling to room temperature (25 °C), the gas flow was purged with He for 30 min, following which the background spectrum was collected. Then, the He flow was switched to a 5 vol% CO in He flow (20 mL min<sup>-1</sup>) which was maintained until saturated adsorption was achieved. The system was purged with He to remove non-adsorbed CO and DRIFT spectra were collected, such that CO adsorption data at room temperature were obtained.

The exposure of Ir NPs was determined by CO and  $H_2$  chemisorption on a Micromeritics AutoChem II 2920 instrument. For the CO (or  $H_2$ ) chemisorption experiment, the sample was pretreated in a  $H_2$  flow at the desired temperature for 60 min, followed by purging with He (or Ar) for 30 min. After cooling

Paper Green Chemistry

down to 50 °C, a 5% CO in He (or 10% H<sub>2</sub> in Ar) was injected into the reactor repeatedly until saturated adsorption is achieved. The dispersion of Ir was determined by assuming the CO/Ru (or H/Ru) adsorption stoichiometry to be 1:1.

#### Catalyst testing

CO<sub>2</sub> hydrogenation reactions were performed in a fixed-bed quartz reactor at atmospheric pressure. Prior to each reaction, the Ir/TiO2 catalyst (0.15 g) was in situ reduced in a H2 flow (20 mL min<sup>-1</sup>) at the desired temperature for 2 h. After the reactor was cooled down, a feed gas with a H2/CO2 ratio of 3.5/  $1 (H_2/CO_2/N_2 = 70/20/10 (v/v/v), N_2 \text{ was used as an internal})$ standard) was introduced into the reactor for CO2 hydrogenation tests. The reactions were carried out at 280 °C and 9000 mL  $g_{cat}^{-1}$  h<sup>-1</sup>. After passing through an ice bath, the gaseous products were analyzed online using an A90 Echrom gas chromatograph equipped with a TDX-01 column connected to a thermal conductivity detector (TCD).

The  $CO_2$  conversion,  $X_{CO_2}$ , was calculated using the follow-

$$X_{\text{CO}_2} = \frac{n_{\text{in}}(\text{CO}_2) - n_{\text{out}}(\text{CO}_2)}{n_{\text{in}}(\text{CO}_2)} = 1 - \frac{A_{\text{out}}(\text{CO}_2)/A_{\text{out}}(\text{N}_2)}{A_{\text{in}}(\text{CO}_2)/A_{\text{in}}(\text{N}_2)},$$

where  $n_{\rm in}({\rm CO_2})$  and  $n_{\rm out}({\rm CO_2})$  refer to the mole number of  ${\rm CO_2}$ at the inlet and outlet, respectively;  $A_{in}(CO_2)$  and  $A_{in}(N_2)$  refer to the chromatographic peak areas of CO2 and N2 in the feed gas; and  $A_{\text{out}}(\text{CO}_2)$  and  $A_{\text{out}}(\text{N}_2)$  refer to the chromatographic peak areas of CO<sub>2</sub> and N<sub>2</sub> in the off-gas.

The reaction rate was calculated as:

Reaction rate = 
$$\frac{\text{GHSV} \times X_{\text{CO}_2} \times \text{CO}_2 \text{ concentration}}{22400 \times \omega_{\text{Ir}}}$$

where GHSV is the gas hourly space velocity and  $\omega_{\rm Ir}$  is the mass fraction of Ir (2.45 wt% as detected by ICP-OES).

For the off-gas consisting only of CO (or CH<sub>4</sub>), the selectivity toward CO (or CH<sub>4</sub>) was assumed to be 100%. For the products in the off-gas consisting of both CO and CH<sub>4</sub>, the selectivity values for CO and  $CH_4$  ( $S_{CO}$  and  $S_{CH_4}$ ) were acquired by a normalization method:

$$S_{\rm CO} + S_{\rm CH_4} = 1, \label{eq:Sco}$$

$$S_{\mathrm{CO}} = f_{\mathrm{CO/CH_4}} imes rac{A_{\mathrm{CO}}}{A_{\mathrm{CH_4}}} imes S_{\mathrm{CH_4}},$$

where  $f_{\rm CO/CH_4}$  is the relative correction factor of CO to CH<sub>4</sub>, which was determined by the calibrating gas; and  $A_{CO}$  and  $A_{\rm CH_{*}}$  refer to the chromatographic peak areas of CO and CH<sub>4</sub>, respectively.

#### Conclusions

In conclusion, we have successfully fabricated a series of highly dispersed, similar sized Ir/TiO<sub>2</sub> catalysts with sintering resistance to high temperature treatment. By varying the reduction temperature to modulate the metal-support interaction, the product selectivity of catalytic CO2 hydrogenation can be tuned from CH<sub>4</sub> to CO. The reduced TiO<sub>x</sub> species that originated from SMSI plays a crucial role in tuning the product selectivity. Ir NPs encapsulated with a TiO<sub>x</sub> coating show a preference for CO production with an inhibition of further hydrogenation, while exposed Ir NPs without TiO<sub>x</sub> promote CH<sub>4</sub> production exclusively. This study provides an understanding of the regulation of CO<sub>2</sub> hydrogenation by SMSI and can serve as an effective approach to tailoring other catalytic processes.

#### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This work was supported by the National Key R&D Program of China (2016YFA0202804), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB36030200), the National Natural Science Foundation of China (21978286, 21925803, 21776269), and the Youth Innovation Promotion Association CAS.

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Green Chemistry Paper

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