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# Synergistic effect between $\text{In}_2\text{O}_3$ and $\text{ZrO}_2$ in the reverse water gas shift reaction†

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Efficient activation of  $\text{CO}_2$  at low temperature was achieved through the interface effect between  $\text{In}_2\text{O}_3$  and  $\text{ZrO}_2$  by their geometric and electronic effects. The results show that  $75\text{In}_2\text{O}_3\text{-}25\text{ZrO}_2$  ( $\text{In}_2\text{O}_3$  :  $\text{ZrO}_2$  molar ratio of 3 : 1), as a catalyst for the reverse water gas shift reaction, can achieve 28%  $\text{CO}_2$  conversion with 96% CO selectivity at 400 °C, 0.1 MPa, a  $\text{H}_2$  :  $\text{CO}_2$  molar ratio of 3 : 1 and a gas hourly space velocity of 10 000  $\text{mL g}^{-1} \text{h}^{-1}$ . *In situ* FTIR experiments provide a basis for clarifying the pivotal role of formate (facilitated at  $\text{In}_2\text{O}_3\text{-ZrO}_2$  interface) in this reaction.

## 1. Introduction

Throughout the course of industrial development, humans have heavily relied on fossil fuels to meet the substantial demand for energy, resulting in a continuous increase in greenhouse gas emissions and exacerbation of climate change.<sup>1</sup> Utilizing carbon dioxide, an abundant and economical carbon resource, to produce high-value-added chemicals or liquid fuels is of significant importance for energy conservation, emissions reduction, and the sustainable utilization of carbon resources.<sup>2</sup> In recent years, carbon capture and utilization (CCU) technology has attracted much attention and is considered as one of the useable ways to reduce  $\text{CO}_2$  emissions.<sup>3–7</sup> The thermal catalytic reduction of  $\text{CO}_2$  refers to the process of converting  $\text{CO}_2$  into hydrocarbons or carbon monoxide (CO) with green hydrogen, typically carried out with the aid of catalysts at elevated temperature.<sup>8</sup> The rapid development of renewable energy lowers the cost of green hydrogen production,<sup>9</sup> prompting the urgent need for catalysts with high activity, selectivity, and stability.

The reverse water gas shift (RWGS) reaction hydrogenates  $\text{CO}_2$  into CO, which can be further used to synthesize methanol, breaking through the thermodynamic equilibrium limit of direct methanol production from  $\text{CO}_2$ ,<sup>10,11</sup> and can also be

combined with Fischer–Tropsch synthesis (FTS) process to prepare useful chemicals such as olefins.<sup>12–15</sup> Whether producing methanol through the CAMERE method (carbon dioxide hydrogenation to form methanol *via* a RWGS reaction) or preparing low-carbon olefins *via* the  $\text{CO}_2$ -FTS method, the RWGS reaction with high CO yield is a crucial step. Therefore, the RWGS reaction is considered as the most promising and prospective pathway in re-utilizing  $\text{CO}_2$ .

Catalysts used in the RWGS reaction can be classified into noble metal catalysts, such as Rh,<sup>16</sup> Ru,<sup>17</sup> and Pt,<sup>18</sup> and non-noble metal catalysts, such as Co,<sup>19</sup> Fe,<sup>20,21</sup> and Mo.<sup>22,23</sup> The noble metal catalysts exhibit outstanding performance due to their effective hydrogen dissociation capabilities, but their high costs and instability (nanoparticle agglomeration) limit their industrial application; the non-noble metal catalysts need high temperature to deliver the same performance as noble metal ones.<sup>24</sup> Therefore, there is of significant importance in developing low-temperature, high-performance catalysts to address these limitations. In recent years, indium oxide ( $\text{In}_2\text{O}_3$ ) has been found as a proficient catalyst for  $\text{CO}_2$  hydrogenation, with its pronounced catalytic activity attributed to the abundant oxygen vacancy ( $\text{O}_v$ ) on its surface.<sup>25–28</sup> Furthermore,  $\text{In}_2\text{O}_3$  can be easily supported and/or modified by promoters to form more  $\text{O}_v$  sites, thereby activating more  $\text{CO}_2$  molecules, and stabilizing surface intermediates near  $\text{O}_v$ .<sup>29–33</sup>

Moreover,  $\text{ZrO}_2$  is also used as catalyst support in RWGS reaction, but its role plays in the reaction is still unclear.<sup>34</sup> Unfortunately, there are relatively few reports related to the synergistic interfacial effect between  $\text{In}_2\text{O}_3$  and  $\text{ZrO}_2$ , hampering the rational design of mixed oxides for the RWGS reaction. For the optimal  $75\text{In}_2\text{O}_3\text{-}25\text{ZrO}_2$  ( $\text{In}_2\text{O}_3$  :  $\text{ZrO}_2$  molar ratio of 3 : 1) with abundant  $\text{In}_2\text{O}_3\text{-ZrO}_2$  interface, 28%  $\text{CO}_2$  conversion and 96% CO selectivity can be achieved at 400 °C, 0.1 MPa,  $\text{H}_2$  :  $\text{CO}_2$  molar ratio of 3 : 1 and GHSV (gas hourly space velocity) of 10 000  $\text{mL g}^{-1} \text{h}^{-1}$ . Control experiments and characterization results testify that the as-formed oxygen

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vacancies ( $O_{vs}$ ) caused by the reduction of  $In_2O_3$  to  $In_2O_{3-x}$  significantly enhance catalytic activity for  $75In_2O_3-25ZrO_2$ . In addition, *in situ* Fourier transform infrared spectroscopy (FTIR) shows that  $HCOO^*$  (formate) plays an important role in this reaction. For  $75In_2O_3-25ZrO_2$  with abundant  $In_2O_3-ZrO_2$  interface,  $HCOO^*$  is easily hydrogenated into CO. However, for  $In_2O_3$ , the content of  $HCOO^*$  is relatively lower, thus contributing to its lower catalytic activity. For  $ZrO_2$ , the  $CO_3^{2-}$  is relatively stable, correlating well with its low catalytic activity. This work elucidates the synergistic effect between mixed  $In_2O_3$  and  $ZrO_2$ , paving a way to design industrial catalyst with abundant  $In_2O_3-ZrO_2$  interface to offer excellent catalytic performance for RWGS reaction.

## 2. Experimental

### 2.1. Catalyst preparation

The mixed In-Zr oxides were synthesized by a co-precipitation method. For instance, for the  $75In_2O_3-25ZrO_2$  ( $In_2O_3:ZrO_2$  molar ratio of 3:1), 1.5612 g  $In(NO_3)_3 \cdot xH_2O$  and 0.3713 g  $Zr(NO_3)_4 \cdot 5H_2O$  were dissolved in 20 mL deionized water, followed by the addition of the mixed solution of  $NH_4OH$  (10 mL, 25 wt% in  $H_2O$ , Alfa Aesar) and ethanol (30 mL, Titan) until the pH reaching 9.2. The resulting slurry was heated to 80 °C with vigorous stirring and aged for 30 min. Then the solid was separated by high-pressure filtration, washed with 500 mL deionized water, dried at 60 °C for 12 h, and calcined at 500 °C (heating rate of ca. 2 °C  $min^{-1}$ ) for 3 h. Other catalysts such as  $In_2O_3$ ,  $ZrO_2$ , and  $aIn_2O_3-bZrO_2$  ( $a$  and  $b$  represent  $In_2O_3$  and  $ZrO_2$  molar ratio ( $a = 25\%$ ,  $50\%$ , and  $75\%$ ,  $b = 1 - a$ )) were prepared using the same method by simply tuning the molar ratio of  $In(NO_3)_3 \cdot xH_2O$  and  $Zr(NO_3)_4 \cdot 5H_2O$ .

### 2.2. Catalyst characterization

The  $N_2$  sorption was conducted using the ASAP 2020 instrument (Mack, USA). The specific surface area ( $S_{BET}$ ) was determined by Brunauer-Emmett-Teller (BET) model and the pore size was calculated by Barret-Joyner-Halenda (BJH) model. The In and Zr loadings were detected by an inductively coupled plasma-atomic emission spectrometry (ICP-AES) at 167–785 nm/725 instrument (Agilent Corporation, USA). The power X-ray diffraction (XRD) patterns of catalysts were obtained on a Rigaku D/Max 2550 VB/PC instrument (Rigaku, Japan) using a scanning rate of 10°  $min^{-1}$ . The fine structures were observed by a transmission electron microscopy (TEM) at an accelerating voltage of 200 kV on JEM-2100 (JEOL, Japan). The energy dispersive X-ray spectroscopy (EDX) was measured by the JEM-2100 (JEOL, Japan) with an amplification of 8000–300 000. X-ray photoelectron spectroscopy (XPS) was measured at ESCALAB 250Xi photoelectron spectrometer (Thermo Fisher Scientific, USA) equipped with an Al-K $\alpha$  X-ray source. All the binding energies were calibrated on the basis of the internal standard of the binding energy of C 1s (284.8 eV). Electron paramagnetic resonance (EPR) spectroscopy was performed using the CIQTEK EPR200-Plus. Spectra were collected accumulating 1 scan for field sweeps of 3250–3850 G at 298 K with a magnetic field

modulation frequency of 100 kHz. The spectrum of an empty tube was subtracted to correct for the background signal.

The experiments of  $H_2$ -temperature programmed reduction ( $H_2$ -TPR) and  $CO_2$ -temperature programmed desorption ( $CO_2$ -TPD) were carried out on a ChemBET Pulsar automatic adsorption apparatus (Quantachrome Company, USA) equipped with a thermal conductivity detector (TCD), and the efflux were monitored by an on-line mass spectrometer (MS, SHP8400PMS-L, Shanghai Sunny Hengping Scientific Instrument Co. Ltd, China). For  $H_2$ -TPR, each catalyst (0.1 g) was pretreated in Ar flow (30 mL  $min^{-1}$ ) at 300 °C for 0.5 h and cooled down to room temperature. Then, the gas was switched to  $H_2/Ar$  flow (10 vol%  $H_2$ , 50 mL  $min^{-1}$ ) and the catalyst was reduced from room temperature to 800 °C at a heating rate of 10 °C  $min^{-1}$ . For  $CO_2$ -TPD, each catalyst (0.1 g) was pretreated in Ar flow (30 mL  $min^{-1}$ ) at 400 °C for 1 h, and then reacted in mixture gas (the molar ratio of  $H_2:CO_2$  is 3:1, 50 mL  $min^{-1}$ ) at 400 °C for 2 h. Then, the catalyst was cooled to 50 °C in the same flow followed by  $CO_2$  (50 mL  $min^{-1}$ ) adsorption at 50 °C for 2 h. After that, the catalyst was flushed in He flow (50 mL  $min^{-1}$ ) for 0.5 h, followed by heated from 50 to 800 °C at a rate of 10 °C  $min^{-1}$ , and signals of  $CO_2$  were monitored by MS on line.

The *in situ* Fourier transform infrared (FT-IR) was conducted on a IRPrestige-21 equipment (Shimadzu, Japan). A resolution of 8  $cm^{-1}$  and scanning times of 50. 50 mg catalyst and 100 mg KBr were pressed into a wafer and placed in the *in situ* chamber. All the samples were pretreated at 400 °C in  $H_2$  flow (37.5 mL  $min^{-1}$ ) for 10 min and cooled to the room temperature to obtain the background spectrum. When the adsorption of  $CO_2$ , the flow was switched to  $CO_2$  (12.5 mL  $min^{-1}$ , 99.99%) at room temperature for 10 min, after that,  $CO_2$  was switched off and the catalyst was maintained at 50 °C for 2 h. Subsequently, catalyst was purged with a He flow (30 mL  $min^{-1}$ ) for 5 minutes and then raised from 50 to 400 °C, with the spectra were collected. After raising to 400 °C, the flow was switched to  $H_2$  for 10 s,  $H_2$  was switched off and the spectra was collected at 0.5 MPa. When the co-adsorption of  $CO_2$  and  $H_2$ , the flow was switched to the mixed gas (the molar ratio of  $H_2:CO_2$  is 3:1, 50 mL  $min^{-1}$ ). The temperature was raised from 100 to 400 °C and the spectra were collected.

### 2.3. Catalytic evaluation

In this work, a continuous fixed-bed reactor was used to evaluate the performance of catalysts. Typically, 0.3 g catalyst was loaded into a reactor with an inner diameter of 7 mm and the length of 700 mm.  $H_2$  (36 mL  $min^{-1}$ ),  $CO_2$  (12 mL  $min^{-1}$ ), and Ar (2 mL  $min^{-1}$ ) was controlled by mass flow controllers, forming a  $H_2/CO_2/Ar$  (molar ratio of 72/24/4) mixture and passing through the catalyst bed. The Ar was used as the internal standard gas. Then, the temperature was successively raised from room temperature to 400 °C and maintained for 2 h. The effluent was analyzed by online gas chromatography (GC7900), equipped with a thermal conductivity detector (TCD) and TDX-1 column. The  $CO_2$  conversion ( $X_{CO_2}$ ), CO selectivity ( $S_{CO}$ ), CO yield ( $Y_{CO}$ ) and  $CH_4$  selectivity ( $S_{CH_4}$ ) were calculated as follows:



$$X_{\text{CO}_2} = \frac{\text{CO}_2^{\text{in}} - \text{CO}_2^{\text{out}}}{\text{CO}_2^{\text{in}}} \times 100\% \quad (1)$$

$$S_{\text{CO}} = \frac{\text{CO}^{\text{out}}}{\text{CO}_2^{\text{in}} - \text{CO}_2^{\text{out}}} \times 100\% \quad (2)$$

$$Y_{\text{CO}} = X_{\text{CO}_2} \times S_{\text{CO}} \quad (3)$$

$$S_{\text{CH}_4} = \frac{\text{CH}_4^{\text{out}}}{\text{CO}_2^{\text{in}} - \text{CO}_2^{\text{out}}} \times 100\% \quad (4)$$

$\text{CO}_2^{\text{in}}$  and  $\text{CO}_2^{\text{out}}$  represent the concentration of  $\text{CO}_2$  at the inlet and outlet, respectively;  $\text{CO}^{\text{out}}$  represents the concentration of CO at the outlet;  $\text{CH}_4^{\text{out}}$  represent the concentration of CH<sub>4</sub> at the outlet.

### 3. Results and discussion

#### 3.1. Structures and chemical states of fresh catalysts

Five  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts were prepared by the co-precipitation method, varying the molar content of  $\text{In}_2\text{O}_3$  of 0, 25%, 50%, 75% and 100%. The inductively coupled plasma-atomic emission spectrometry (ICP-OES) measurements confirmed that In and Zr contents were almost identical to the theoretical value. Adding  $\text{ZrO}_2$  to  $\text{In}_2\text{O}_3$  will slightly increase the specific surface area (Table S1<sup>†</sup>), but the specific surface area of  $75\text{In}_2\text{O}_3$ - $25\text{ZrO}_2$  is close to that of  $\text{In}_2\text{O}_3$ , albeit the catalyst area is not the key factor determining catalytic activity.<sup>35</sup> Moreover, the type IV hysteresis loop testifies the mesoporous structure of this series of catalysts (Fig. S1<sup>†</sup>). TEM images of this series of catalysts show the similar morphologies, with the diameter of 8–15 nm (Fig. S2<sup>†</sup>).

For  $75\text{In}_2\text{O}_3$ - $25\text{ZrO}_2$ , the average particle size is 10.0 ± 1.4 nm, and the HRTEM images illustrate the lattice distances of 0.292, 0.275, and 0.297 nm, corresponding to the  $\text{In}_2\text{O}_3$ (222),  $\text{In}_2\text{O}_3$ (321), and  $t$ - $\text{ZrO}_2$ (101) planes, respectively (Fig. S3a and b<sup>†</sup>). The STEM-EDX mapping images show that In and Zr elements are randomly distributed on the catalyst surface (Fig. S3c and d<sup>†</sup>), forming abundant  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  interface and tentatively contributing to excellent catalytic performance.

X-ray diffraction (XRD) was used to figure out the effect of Zr modification on bulk structure. The XRD patterns in Fig. S4a,<sup>†</sup> display that the pure  $\text{ZrO}_2$  (*i.e.*,  $0\text{In}_2\text{O}_3$ - $100\text{ZrO}_2$ ) prefers to crystallize to its thermodynamically stable monoclinic structure; the presence of In steers the growth of  $\text{ZrO}_2$  toward metastable tetragonal phase,<sup>28</sup> suggesting that partial In is incorporated into the  $\text{ZrO}_2$  lattice in the form of In–O–Zr bond, as evidenced by the HRTEM image of  $75\text{In}_2\text{O}_3$ - $25\text{ZrO}_2$  sample.<sup>36</sup> The transition from In–O–In bond to In–O–Zr bond should greatly improve the  $\text{CO}_2$  conversion and CO selectivity of  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts (see the results in Section 3.2). Owing to the fact that the lattice parameters of cubic  $\text{In}_2\text{O}_3$  (JCPDS card 06-0416) and  $t$ - $\text{ZrO}_2$  (JCPDS card 37-1413) are akin, their XRD patterns are virtually identical. However, as shown in Fig. S4b,<sup>†</sup> the diffraction peak moves from  $30.167^\circ$  ( $t$ - $\text{ZrO}_2$ (111)) to  $30.580^\circ$  ( $c$ - $\text{In}_2\text{O}_3$ (222)) with the increase of  $\text{In}_2\text{O}_3$  content, and such tiny peak shift confirms the generation of  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  solid solution.

The surface chemical states of  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts were characterized by XPS (Fig. 1) and EPR (Fig. S6<sup>†</sup>). The symmetric binding energy peaks at ~452 and ~444.3 eV testify that In species exists in the form of  $\text{In}^{3+}$ .<sup>37</sup> With the increase of  $\text{In}_2\text{O}_3$  content, the binding energy of  $\text{In}^{3+}$  decreases slightly, indicating the electron transfer from Zr to In.<sup>36</sup> The symmetric binding energy peaks at ~184.5 and ~182.0 eV testify that Zr species exists in the form of  $\text{Zr}^{4+}$ .<sup>38</sup> For  $50\text{In}_2\text{O}_3$ - $50\text{ZrO}_2$  and  $75\text{In}_2\text{O}_3$ - $25\text{ZrO}_2$ , the binding energies of Zr are higher than that of  $25\text{In}_2\text{O}_3$ - $75\text{ZrO}_2$ , also coinciding with the electron transfer. For the O 1s XPS spectra, the major peak at 529.5–531.0 eV corresponds to lattice oxygen, the peak at 531.0–532.0 eV to  $\text{O}_v$ , and the one at 532.5–533.0 eV to surface OH.<sup>39</sup> Obviously, with the increase of  $\text{In}_2\text{O}_3$  content, the  $\text{O}_v$  content increases progressively. Fig. S5<sup>†</sup> shows that there is a positive correlation between the CO STY (space-time yield) and the oxygen vacancy concentration, which means that the  $\text{O}_v$  may play an important role in the RWGS reaction. Furthermore, the EPR results in Fig. S6<sup>†</sup> reveals a signal of  $g = 1.890$  for fresh  $\text{In}_2\text{O}_3$ , which implies that the surface vacancies exist on  $\text{In}_2\text{O}_3$ .<sup>40</sup> Pure  $\text{ZrO}_2$  sample exhibits an isotropic EPR signal at  $g = 1.973$ , which is assigned to the bulk  $\text{Zr}^{3+}$  ions located at axially symmetric sites. The  $75\text{In}_2\text{O}_3$ - $25\text{ZrO}_2$  demonstrates a prominent signal that can be attributed to unpaired electrons trapped in symmetric site at  $g$

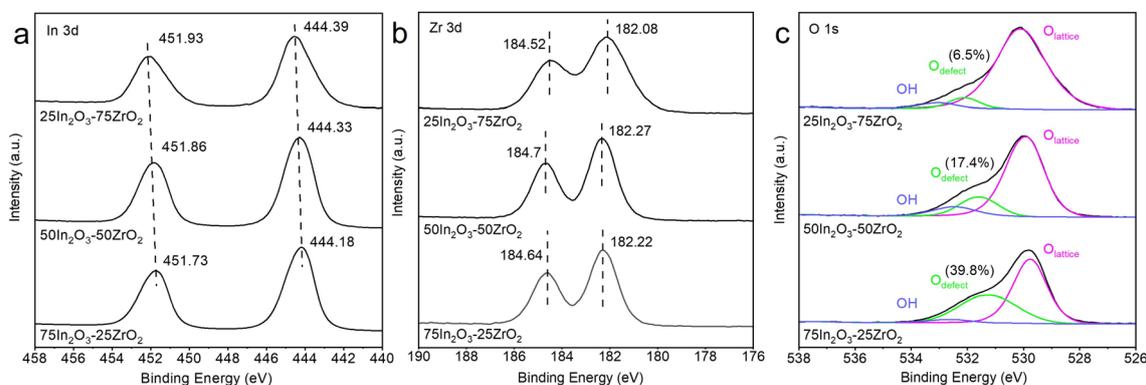


Fig. 1 XPS spectra of (a) In 3d, (b) Zr 3d, and (c) O 1s for the  $25\text{In}_2\text{O}_3$ - $75\text{ZrO}_2$ ,  $50\text{In}_2\text{O}_3$ - $50\text{ZrO}_2$  and  $75\text{In}_2\text{O}_3$ - $25\text{ZrO}_2$  catalyst.



= 2.004, which is always typically assigned to oxygen vacancies.<sup>41</sup> This means the synergistic effect between In<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> in 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> solid solution is beneficial to produce new oxygen vacancies at  $g = 2.004$ , which is in line with the XPS result.

H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) tests were conducted to determine the reactivity of the In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst toward H<sub>2</sub> activation in the temperature range of 50–800 °C, as shown in Fig. S7a.† The H<sub>2</sub>-TPR profiles revealed that reduction temperature of bulk In<sub>2</sub>O<sub>3</sub> in In<sub>2</sub>O<sub>3</sub> and 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> are 662 °C and 697 °C respectively, while the reduction temperature of surface In<sub>2</sub>O<sub>3</sub> are 189 °C and 225 °C respectively. However, the H<sub>2</sub>-TPR of ZrO<sub>2</sub> demonstrates no significant H<sub>2</sub> consumption, which means the neglectable reducibility of ZrO<sub>2</sub>. Interestingly, for 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub>, the reduction signals of surface and the bulk In<sub>2</sub>O<sub>3</sub> are located at a higher temperature than that of pure In<sub>2</sub>O<sub>3</sub> catalyst, hinting a stronger interaction between In<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.<sup>29</sup> This also shows the increasing O<sub>v</sub> content over 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> catalyst, which is in accordance with the XPS result and the prominent catalytic activity.<sup>42</sup>

CO<sub>2</sub> temperature programmed desorption (CO<sub>2</sub>-TPD) was conducted to further investigate the CO<sub>2</sub> adsorption behaviour on the In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst, as shown in Fig. S7b.† The profiles exhibit several significant CO<sub>2</sub> evolution signals from the ZrO<sub>2</sub> and 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> catalyst in the temperature range of 134–220, 273–315 and 396–477 °C. While the signal of CO<sub>2</sub> adsorbed on pure In<sub>2</sub>O<sub>3</sub> are not detectable. The signal peak around 153 °C belongs to the physisorption of CO<sub>2</sub>. Other signal peaks belong to the chemically absorbed CO<sub>2</sub> on the H<sub>2</sub>-induced oxygen vacancy sites (O<sub>v</sub>).<sup>42</sup> Additionally, CO<sub>2</sub>-TPD has been widely used to measure the surface basicity of catalysts, and high desorption temperature promised a strong basic site.<sup>43</sup> Compared with ZrO<sub>2</sub> catalyst, the CO<sub>2</sub> desorption peak of 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> catalyst shift to the higher temperatures of 315 °C and 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> catalyst have strong site at around 450 °C. Specifically, the addition of In enhances the strength of CO<sub>2</sub> adsorption on these sites, owing to the increase in basic intensity.<sup>42</sup> The characterization results of H<sub>2</sub>-TPR and CO<sub>2</sub>-TPD consistently confirm that In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> interface benefits the formation of oxygen vacancies, thus enhancing the ability of 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> catalyst to CO<sub>2</sub> adsorption and H<sub>2</sub> activation.

### 3.2. Catalytic performance

CO<sub>2</sub> hydrogenation mainly involves the following three reactions (5)–(7) to produce three products of CO, CH<sub>4</sub> and CH<sub>3</sub>OH, respectively.

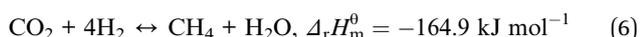


Fig. 2a shows the CO<sub>2</sub> conversion, CO selectivity, and CO yield over the five catalysts. The catalytic performance of pure ZrO<sub>2</sub> (*i.e.*, 0In<sub>2</sub>O<sub>3</sub>-100ZrO<sub>2</sub>) is extremely poor, with CO<sub>2</sub> conversion of only 4% and CO selectivity of only 53%, while the

pure In<sub>2</sub>O<sub>3</sub> (*i.e.*, 100In<sub>2</sub>O<sub>3</sub>-0ZrO<sub>2</sub>) gives higher CO<sub>2</sub> conversion of 23.5% and CO selectivity of 95.8%. Interestingly, the In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts (*i.e.*, 25In<sub>2</sub>O<sub>3</sub>-75ZrO<sub>2</sub>, 50In<sub>2</sub>O<sub>3</sub>-50ZrO<sub>2</sub>, and 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub>) all offers CO selectivity above 92%, with volcano evolution of CO<sub>2</sub> conversion. Most notably, the 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> offers the highest CO selectivity of 96% and highest CO<sub>2</sub> conversion of 28%. Due to a pronounced synergistic effect between ZrO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>, the In-Zr interface within the bimetallic oxides augments the density of O<sub>v</sub> on the In<sub>2</sub>O<sub>3</sub> surface, thereby significantly enhancing the adsorption and hydrogenation capacities towards CO<sub>2</sub>. In addition, no methane can be detected, and a small amount of methanol was the only by-product.

The influence of reaction temperature, pressure, and gas hourly space velocity (GHSV) on catalytic performance is exhibited in Fig. 2b, c and S8.† At 0.1 MPa, and GHSV of 10 000 mL g<sup>-1</sup> h<sup>-1</sup>, with the temperature rising from 300 to 500 °C, CO<sub>2</sub> conversion increases from 4% to 44%, and the highest CO selectivity is 96% at 400 °C. At 400 °C, and GHSV of 10 000 mL g<sup>-1</sup> h<sup>-1</sup>, with the pressure increasing from 0.1 to 4 MPa, CO<sub>2</sub> conversion slightly increases from 28% to 29%, but CO selectivity decreases from 96% to 85% (with the formation of new by-product CH<sub>4</sub>), because high reaction pressure is beneficial to CO<sub>2</sub> methanation reaction.<sup>44</sup> Moreover, at 0.1 MPa, and 400 °C, CO<sub>2</sub> conversion decreases from 35% to 27.7% with increasing GHSV from 6000 to 14 000 mL g<sup>-1</sup> h<sup>-1</sup>, while the maximum CO selectivity is 94% at the GHSV of 10 000 mL g<sup>-1</sup> h<sup>-1</sup>. Hence, the optimized reaction condition is as follows: 0.1 MPa, 400 °C and GHSV of 10 000 mL g<sup>-1</sup> h<sup>-1</sup>. For the best catalyst 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub>, under the best reaction conditions, the CO<sub>2</sub> conversion and CO selectivity are 28% and 96% in the 200 h-test. However, for In<sub>2</sub>O<sub>3</sub>, the conversion decreases from 26% to 21%. Compared with pure In<sub>2</sub>O<sub>3</sub>, the stability of mixed oxides is obviously enhanced. Hence, the In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> interface is of great importance in improving and maintaining catalytic activity (Fig. 2d). We compared the catalyst 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> with other catalysts including non-noble metal and noble metal catalysts in the RWGS reaction in Table S3.† CO<sub>2</sub> conversion, CO selectivity and STY of 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> are very promising. Notably, the STY of 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> is higher than other catalysts (apart from Ag/Al<sub>2</sub>O<sub>3</sub>). Furthermore, compared with noble metal catalysts, In-based catalysts have lower cost and more prospects in industry applications.

### 3.3. Surface intermediates and reaction mechanism

*In situ* FTIR was used to investigate the evolution of key surface intermediates for RWGS reaction, and the wavenumbers of the intermediates are summarized in Table S4.†<sup>33,34,36,37,39,45-55</sup> Firstly, the three catalysts (75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>) were placed into the chamber and reduced with hydrogen at 400 °C. Subsequently, CO<sub>2</sub> was introduced into the chamber for adsorption. Finally, the gaseous CO<sub>2</sub> was purged by He flow and the spectra were collected from 50 to 400 °C (Fig. 3). For 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> (Fig. 3a), the following characteristic bands can be observed: bi-HCOO\* (bidentate formate, at 1350, 1589, 2873 and 2967 cm<sup>-1</sup>);<sup>33,36,39,46,48,50,52-55</sup> b-\*OCH<sub>3</sub> (bridged methoxy, at





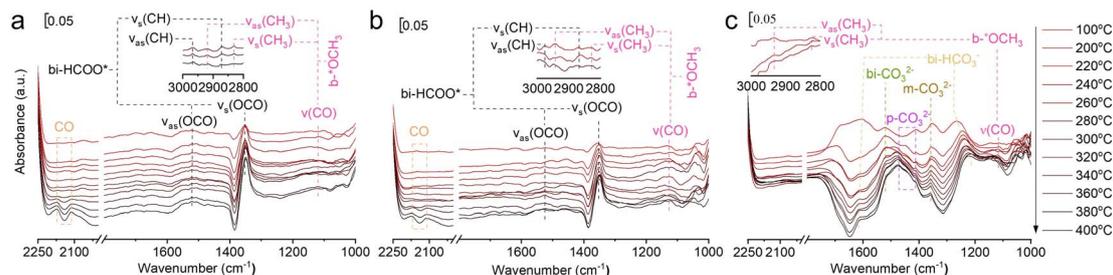


Fig. 4 *In situ* FTIR spectra of the reaction of CO<sub>2</sub> and H<sub>2</sub> over (a) 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub>, (b) In<sub>2</sub>O<sub>3</sub>, and (c) ZrO<sub>2</sub>.

FTIR (Fig. 4). For 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub>, the characteristic band of CO is observed at 320 °C ( $\nu(\text{CO}) = 2111.1$  and  $2170 \text{ cm}^{-1}$ ). However, for In<sub>2</sub>O<sub>3</sub>, CO starts to appear at 360 °C, corresponding well with its lower catalytic activity. For ZrO<sub>2</sub>, the characteristic bands of CO are not observed, showing that bi-HCO<sub>3</sub><sup>-</sup>, bi-CO<sub>3</sub><sup>2-</sup>, m-CO<sub>3</sub><sup>2-</sup>, and p-CO<sub>3</sub><sup>2-</sup> can't be hydrogenated easily.<sup>48</sup> Lastly, for all the three catalysts, b-OCH<sub>3</sub><sup>\*</sup> is also observed, but this species could only be hydrogenated to CH<sub>4</sub> at relative higher 0.5 MPa, thus excluding the role of OCH<sub>3</sub><sup>\*</sup> playing under the reaction conditions (Fig. S9†). But the CH<sub>4</sub> is not formed in the real fixed-bed reaction process, which is likely caused by the different conditions between *in situ* FTIR and real reaction process.

Combined with the above analyses, it can be suggested that CO<sub>2</sub> hydrogenation on the In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst through HCOO\* intermediates (Scheme S1†). H<sub>2</sub> adsorbed on the exposed surface of In<sub>2</sub>O<sub>3</sub> crystal to form H<sub>2</sub><sup>\*</sup>, and then formed H<sub>in</sub><sup>\*</sup> and H<sub>O</sub><sup>\*</sup> at In site and O site, respectively. At the same time, CO<sub>2</sub> is adsorbed on a base on the surface of the composite oxide, activated by oxygen vacancy, and then combined with activated H<sub>in</sub><sup>\*</sup> to form formate intermediate (HCOO\*). HCOO\* interacts with the site of ZrO<sub>2</sub>, undergoes the cleavage of C-O and C-H bonds, and forms O-H bonds at the same time, producing CO\* and OH\*, and CO\* desorbs to produce CO.<sup>33,37</sup> In this case, ZrO<sub>2</sub> can not only modify In<sub>2</sub>O<sub>3</sub>, but also serve as an active site. In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> constitutes a bimetallic In-Zr oxide catalyst system.

## 4. Conclusions

In this work, the optimal 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> and the contrastive In<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> were prepared by the coprecipitation method, and 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> exhibits excellent 28% conversion and 96% selectivity in the RWGS reaction under the best reaction conditions (400 °C, 0.1 MPa, H<sub>2</sub> : CO<sub>2</sub> molar ratio of 3 : 1 and gas hourly space velocity of  $10\,000 \text{ mL g}^{-1} \text{ h}^{-1}$ ). XRD and STEM-EDX show that the In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> solid solution is formed, and XPS testifies that the electron transfer effect plays an important role in this reaction. *In situ* FTIR shows that: for 75In<sub>2</sub>O<sub>3</sub>-25ZrO<sub>2</sub> with abundant In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> interface, HCOO\* is easily hydrogenated into CO; however, for In<sub>2</sub>O<sub>3</sub>, the content of HCOO\* is relatively lower, thus contributing to its lower catalytic activity; for ZrO<sub>2</sub>, the CO<sub>3</sub><sup>2-</sup> is relatively stable, correlating well with its low catalytic activity. This work definitely testifies the pivotal role of HCOO\* in the RWGS reaction, but also paves a way to design bimetal oxide catalyst with excellent catalytic performance for RWGS reaction.

## Conflicts of interest

The authors declare that there is no conflict of interest.

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