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# Improvement in the activity of Ru/ZrO<sub>2</sub> for CO<sub>2</sub> methanation by the enhanced hydrophilicity of zirconia



# Menghui Liu<sup>a</sup>, Rui Zou<sup>a</sup>, Chang-jun Liu<sup>a,b,\*</sup>

<sup>a</sup> School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China
 <sup>b</sup> Collaborative Innovation Center of Chemical Science & Engineering, Tianjin University, Tianjin 300072, China

pathway.

A R T I C L E I N F O Keywords: CO <sub>2</sub> methanation Hydrophilicity Plasma Ruthenium Zirconia	A B S T R A C T			
	Increasing interests in the supported Ru catalysts for $CO_2$ methanation can be recently found in the literature. In this work, we demonstrated that the enhanced surface hydrophilicity of $ZrO_2$ via air plasma treatment has significant effects on the properties of Ru/ZrO <sub>2</sub> catalyst for $CO_2$ methanation. At the same $CO_2$ conversions, the reaction temperature over the catalysts on $ZrO_2$ with enhanced hydrophilicity is $20-70$ °C lower than those on untreated $ZrO_2$ . The catalyst characterization confirms that the enhanced hydrophilicity leads to more hydroxyl groups and oxygen vacancies on the support, which further promotes $CO_2$ adsorption and activation, facilitating the conversion of $CO_2$ to $HCO_3^*$ and $HCOO^*$ in formate pathway. The enhanced hydrophilicity also causes a high Ru dispersion with stronger electronic interaction between Ru and $ZrO_2$ , which forms more interfacial active sites and improves the adsorption and dissociation of $H_2$ , promoting the linear- $CO-Ru^0$ adsorption in $CO^*$			

# 1. Introduction

The utilization of carbon dioxide has become a hot topic with the development of the technologies of CO<sub>2</sub> capture and renewable energies. There are many options for the CO<sub>2</sub> utilization [1–5]. Among them, CO<sub>2</sub> hydrogenation to methane, or CO<sub>2</sub> methanation, or Sabatier reaction (CO<sub>2</sub> + 4 H<sub>2</sub>  $\pm$  CH<sub>4</sub> + 2 H<sub>2</sub>O (g),  $\Delta G^{\circ}_{298 \text{ K}} = -114.0 \text{ kJ/mol}$ ;  $\Delta H^{\circ}_{298 \text{ K}} = -165.0 \text{ kJ/mol}$ ), draws significantly increasing interests since it is promising for CO<sub>2</sub> utilization in large scales [3,6]. This reaction can be used to produce synthetic natural gas for those regions with the need of clean fuel. The established transportation pipeline for natural gas can be applied for the potential CO<sub>2</sub> methanation at the remote site. CO<sub>2</sub> methanation is also promising for the energy storage.

 $\rm CO_2$  methanation is an exothermal reaction. The low reaction temperature is theoretically suitable for the reaction. However, there is a kinetic limitation for  $\rm CO_2$  methanation. To speed up the reaction, some high reaction temperatures are normally required. At the elevated temperatures, a competitive endothermic reverse water gas shift (RWGS) reaction ( $\rm CO_2 + H_2 \rightleftharpoons \rm CO + H_2O$  (g),  $\Delta \rm H^\circ_{298~K} = 41.2~kJ/mol)$  exists, causing the formation of carbon monoxide. An active catalyst is therefore needed for  $\rm CO_2$  methanation at sufficiently low reaction temperatures.

Various metal catalysts, normally supported by the oxides, have been exploited for CO<sub>2</sub> methanation. Among these catalysts, nickel catalysts are the most investigated ones [7–9]. Recently, increasing publications can be found in the literature on the supported ruthenium (Ru) catalysts for CO<sub>2</sub> methanation. The Ru catalyst is cheaper than other noble metal catalysts like palladium. Because of its high ability in not only hydrogen dissociation but also the binding with carbon monoxide, the supported Ru catalyst normally possesses high methane selectivity and high stability for CO<sub>2</sub> methanation. As the supported nickel catalyst [3], the size of the Ru catalyst has a significant influence on CO<sub>2</sub> methanation. Ma and Wang [10] found that the oxygen vacancy (O<sub>v</sub>) of CeO<sub>2</sub> has an influence on the interaction between the Run cluster and CeO<sub>2</sub> by changing the Ru-O bond number. They found the single atom Ru catalyst is not favorable for CO<sub>2</sub> methanation but the Ru<sub>4</sub> catalyst has high activity. Prof. Hensen and his co-workers [11] also found that Ru<sub>1</sub>/CeO<sub>2</sub> is only active for RWGS reaction. They confirmed that the small Ru clusters have strong H<sub>2</sub> adsorption ability, which causes higher activity for CO<sub>2</sub> methanation over the Ru clusters on CeO2. Kwak et al. [12] observed that, at the Ru loadings below or equal to 0.5 %, CO is the main product from RWGS reaction with the atomically dispersed Ru as active species on the alumina support. At higher metal loading, the Ru metallic cluster is generated with increasing methane selectivity. Abe et al. [13]

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<sup>\*</sup> Corresponding author at: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China. *E-mail address*: cjl@tju.edu.cn (C.-j. Liu).

prepared a highly dispersed Ru catalyst with a narrow particle-size distribution and a mean diameter of *ca*. 2.5 nm on anatase  $TiO_2$  using a sputtering method. At ~160 °C, a 100 % yield of methane was reported for  $CO_2$  methanation. Liang *et al.* [14] mixed rutile  $TiO_2$  and palygorskite via a strong electrostatic absorption method. The abundant hydroxyl (OH\*) groups of palygorskite lead to the formation of highly dispersed Ru nanoparticles with 100 % selectivity of methane and high stability during a 60-hr catalytic test at 450 °C.

The surface hydroxyl species on the support can also directly involve in the hydrogenation reactions and improve the performance of the supported Ru catalyst for CO<sub>2</sub> methanation [15–20]. Wang et al. [21] confirmed that Ce<sup>3+</sup>, surface hydroxyl, and oxygen vacancy participate in the catalytic process via the formate pathway in Ru/CeO2 catalyst, while the oxygen vacancy catalyzes the dissociation of formate to methanol, which is the rate-determining step. The further hydrogenation of methanol causes the formation of methane. The hydrogen-spillover effect of metallic Ru is beneficial to the attack of hydrogen atoms on the Ce-O bond of the substrate surface. The oxygen vacancy of Ru/CeO<sub>2</sub> catalyzes the rate-determining step with a much lower activation temperature compared with  $Ru/\alpha$ -Al<sub>2</sub>O<sub>3</sub> (125 vs 250) °C). And,  $Ru/\alpha$ -Al<sub>2</sub>O<sub>3</sub> takes carboxylic route for CO<sub>2</sub> methanation without oxygen vacancy [21]. Wang *et al.* [22] prepared and studied the Ru/CeO2, Ru/SiO2, Ru/γ-Al2O3 and Ru/MgO catalysts for CO2 methanation. They demonstrated that Ru/CeO2 exhibits a higher CO2 conversion (up to 86 %) and a higher methane selectivity (up to 100 %) with excellent stability because of the synergy of abundant weak basic sites and oxygen vacancies. Chen et al. [23] found that the charge transfer from the oxygen vacancies of ZrO<sub>2</sub> to Ru can modify the electronic states of atoms around Ru interface. An enhanced activity with 100 % selectivity of methane was thus achieved for CO<sub>2</sub> methanation. Cisneros et al. [24] investigated the MgO modification for the improved activity of  $\rm Ru/ZrO_2.$  They confirmed that the replacement of  $\rm Zr^{4+}$  by  $\rm Mg^{2+}$  in the ZrO<sub>2</sub> lattice helps the formation of oxygen vacancies and facilitates the electron transfer from oxygen vacancies to the interfacial Ru sites. This improves the activation of hydrogen and weakens the adsorption of the adsorbed bidentate formate (b-HCOO<sub>ads</sub>), leading to its decomposition to CO<sub>ads</sub> with further hydrogenation to methane at the Ru-support perimeter.

The reported works have demonstrated that the oxide supported Ru catalyst is very promising for  $CO_2$  methanation with high activity and stability. However, the study of supported Ru catalyst for  $CO_2$  methanation is still in the early stage. Many fundamental issues are to be investigated. In this work, we attempted to investigate the effect of hydrophilicity of zirconia on Ru/ZrO<sub>2</sub> catalyst for  $CO_2$  methanation. We confirmed that the enhanced hydrophilicity of zirconia leads to improved Ru dispersion with the reduced catalyst size and strong electronic metal-support interaction, which significantly improves the activity of the Ru/ZrO<sub>2</sub> catalyst for  $CO_2$  methanation. The increased hydroxyl groups help the reaction via formate pathway, while the improvement of Ru dispersion favors the CO hydrogenation pathway, compared to the Ru/ZrO<sub>2</sub> catalyst with no enhanced hydrophilicity.

#### 2. Materials and methods

# 2.1. Preparation of the catalysts

Because the plasma treatment normally leads to an increase in the specific surface area of the support, a commercial zirconia (ZrO<sub>2</sub>) ( $\geq$  99 % in purity; Kermel, China) with a low specific surface area (3.1 m<sup>2</sup> g<sup>-1</sup>) was thus chosen as the catalyst support, in order to reduce the potential influence of the surface area change of ZrO<sub>2</sub>. To improve the hydrophilicity of zirconia, a dielectric barrier discharge (DBD) plasma treatment was employed with air as the plasma forming gas. The DBD plasma treatment is a rapid, convenient and effective approach to enhance hydrophilicity with no need of any hazardous chemicals. As

shown in Figure S1, the DBD plasma reactor consists of two steel plate electrodes, attached by the dielectric quartz plates (to form the quartz chamber). The ZrO<sub>2</sub> powder (1.0 g) was placed on the lower quartz plate. The diameter of the steel plate electrodes is 90 mm, while the thickness and diameter of the quartz plates are 2.5 and 50 mm. The discharge gap width between two quartz plates is 8 mm. To generate DBD plasma, a high-voltage generator was used (CTP-2000 K; Corona Laboratory, Nanjing, China). The plasma is initiated at room temperature and operated at atmospheric pressure. Because the plasma treatment causes an increase in the bulk temperature, it is intermittently operated. After one treatment for three minutes, the plasma reactor was cooled down to room temperature. Each sample was treated for 20 times. The details for the DBD plasma operation can be found in our previous works [7,25,26]. The DBD plasma treated ZrO<sub>2</sub> is assigned as DBD-ZrO<sub>2</sub> with a surface area of 4.5 m<sup>2</sup> g<sup>-1</sup>. For comparison purposes, the commercial ZrO<sub>2</sub> sample without the DBD plasma treatment has also been used as the catalyst support. The commercial ZrO2 sample is directly named as ZrO<sub>2</sub>.

The ZrO<sub>2</sub> supported Ru catalysts were prepared by wet impregnation. To do so, ZrO2 was added into the distilled water. The obtained mixture was kept in an ultrasonic bath for 1 h. Ruthenium (III) chloride (RuCl<sub>3</sub>·3 H<sub>2</sub>O) with a concentration of 0.01 g mL<sup>-1</sup> was then added into the solution with ZrO<sub>2</sub>. The mixture was treated in the ultrasound bath for another 2 hrs at room temperature. After that, a solution of dimethylamine borane (DMAB) (≥98 %; J&K Scientific) aqueous solution was added dropwise to the solution of RuCl<sub>3</sub> and ZrO<sub>2</sub> for the prereduction of the ruthenium ion in order to avoid the loss of Ru ion by subsequent processing. The mixture was ultrasound treated for 3 hrs at room temperature. Vacuum filtration was then carried out. The obtained catalyst was washed with water. After that, it was dried overnight at 40 °C under vacuum condition. Before the reaction, the catalyst was further reduced by flowing  $H_2$  (> 99.99 %; supplied by Air Liquide) with a flow rate of 40 mL min<sup>-1</sup> at 200 °C for 1 h. After hydrogen reduction, the catalysts are denoted as 1 %Ru/DBD-ZrO2 and 1 %Ru/ZrO2, respectively. The catalysts with 0.5 wt% and 2 wt% loading of Ru were also prepared to study the effect of the Ru loading. They are named as 0.5 % Ru/DBD-ZrO2 and 2 %Ru/DBD-ZrO2.

# 2.2. Characterizations

The surface hydrophilicity was analyzed by a contact angle measurement (FCA2000A5, Afeschina, Shanghai, China). Brunauer-Emmett-Teller (BET) surface area was determined by N<sub>2</sub> adsorption/desorption isotherms at 77 K, obtained with a BELSORP-miniX instrument. The reduced sample was degassed under vacuum at 200 °C for 8 hrs prior to the measurement. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation.

An inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 720ES) was used to test the actual loading of Ru nanoparticles.

Ultrahigh vacuum-Fourier transform infrared (UHV-FTIR) spectroscopy was employed to investigate the surface OH\* species using a Bruker VERTEX 80 v FT-IR system. The purpose of the use of UHV condition is to completely eliminate the interference of the atmospheric moisture in the infrared light path. The spectral range is from 8000 to 350 cm<sup>-1</sup>.

The morphology of the catalyst was observed by a JEM-F200 transmission electron microscopy (TEM) microscope. To do so, the reduced sample was pre-dispersed into an ethanol solution and then dropwise added to a clean copper grid prior to the analysis. The energy dispersive X-ray (EDX) element mapping was performed at 200 kV to investigate element distribution.

X-ray diffraction (XRD) analyses were operated using a Smartlab XRD diffractometer with Cu K $\alpha$  radiation and a scanning rate of  $2^\circ$  min^{-1}.

Quasi in-situ X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher ESCALAB-250Xi spectrometer with



**Fig. 1.** (a, b) Contact angles of water droplets on the DBD-ZrO<sub>2</sub> and ZrO<sub>2</sub> supports. (c) UHV-FTIR spectra of ZrO<sub>2</sub>, DBD-ZrO<sub>2</sub>, 1 %Ru/ZrO<sub>2</sub> and 1 %Ru/DBD-ZrO<sub>2</sub> at room temperature. (d) XRD patterns of ZrO<sub>2</sub>, DBD-ZrO<sub>2</sub>, 1 %Ru/ZrO<sub>2</sub>, 1 %Ru/ZrO<sub>2</sub>, 1 %Ru/ZBD-ZrO<sub>2</sub> and 2 %Ru/DBD-ZrO<sub>2</sub>. (e, f) Schematic representatives of the effect of the ZrO<sub>2</sub> hydrophilicity on the preparation of Ru/DBD-ZrO<sub>2</sub> and Ru/ZrO<sub>2</sub>.

monochromatic Al K $\alpha$  ( $h\nu = 1486.6$  eV) as the excitation source. The catalyst powder after chemical reduction was pressed on an aluminum plate and then loaded into the sample chamber. After that, the sample was firstly reduced under a pure H<sub>2</sub> at 200 °C for 1 hr. The feed gas of 16 % CO<sub>2</sub>, 64 % H<sub>2</sub>, and 20 % N<sub>2</sub> was switched into the reaction cell. The chamber was then heated to 350 °C. After 90 min, the catalyst was transferred to the sample cell for measurement. The binding energy of C 1 s (284.8 eV) was used as a reference for calibration.

The *ex-situ* XPS analyses of the supports were performed on a K-Alpha+ spectrometer (ThermoFisher Scientific) with monochromatic Al K $\alpha$  radiation as the excitation source. The binding energies were also calibrated by the C 1 s peak at 284.8 eV.

Raman spectra were collected on a laser confocal Raman microscopy (LabRAM HR Evolution) with a 532 nm laser source.

 $H_2$  temperature-programmed reduction ( $H_2$ -TPR) was conducted on a Quantachrome ChemBET Pulsar TPR/TPD instrument. During the measurement, the sample (50 mg) without hydrogen reduction was pretreated with helium for 1 hr at 200 °C and then heated from 25 to 900 °C with 10 % H<sub>2</sub>/Ar at a flow rate of 30 mL min<sup>-1</sup> and a heating rate of 10 °C min<sup>-1</sup>. The thermal conductivity detector (TCD) was used to analyze the effluent gas.

CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) was also carried out on the same instrument for H<sub>2</sub>-TPR. The catalyst was reduced in hydrogen for 1 hr at 200 °C before the measurement. CO<sub>2</sub> was then adsorbed at 30 °C for 1 hr. After that, the catalyst was flushed with helium at a rate of 30 mL min<sup>-1</sup> and heated from 50 to 900 °C at a rate of 10 °C min<sup>-1</sup>. The TCD was also used to analyze the effluent gas.

 $\rm H_2$  temperature-programmed desorption mass spectroscopy (H\_2-TPD-MS) analysis was conducted on a Micromeritics AutoChem II 2920 instrument to investigate the effect of oxygen vacancies of ZrO<sub>2</sub> and DBD-ZrO<sub>2</sub> on hydrogen adsorption and dissociation. To do so, the sample was purged at 200 °C under flowing helium, then cooled down to room temperature, followed by the adsorption of 10 % H<sub>2</sub>/Ar for 1 hr. After that, the sample was purged with the flowing helium again for 1 hr

to remove the physically adsorbed hydrogen. The sample was then heated to 900 °C with a heating rate of  $10^{\circ}$  min<sup>-1</sup> under the flowing helium. The MS signals were monitored using a gas analyzer (Omnistar GSD 301, Pfeiffer Vacuum).

CO titration test was used to measure the metal dispersion. To do so, the sample was firstly reduced at 200 °C by pure  $H_2$  for 1 hr. It was then cooled down to room temperature under a flowing helium. After that, a 10 % CO in helium was used to perform the titration procedure several times until a stable CO signal peak appeared.

 $\rm H_2\text{-}D_2$  exchange experiment was conducted in a fixed bed reactor. The effluent was monitored by an on-line mass spectroscopy. Typically, 50 mg sample was loaded in an inert quartz tube and reduced under a flowing pure  $\rm H_2$  with 40 mL min<sup>-1</sup> at 200 °C for 1 hr. After heating to 300 °C, a mixture of 2 mL min<sup>-1</sup> D<sub>2</sub> and 2 mL min<sup>-1</sup> H<sub>2</sub> was pulsed into the reactor and passed through the catalyst bed. The products, HD, H<sub>2</sub> and D<sub>2</sub>, were analyzed by the mass spectrometer.

The *in-situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy analyses were performed using a Nicolet iS50 FT-IR spectrometer (Thermos Scientific), equipped with a MCT detector and a Harrick reaction cell. Before the *in-situ* DRIFT measurement, the catalyst was reduced for 1 hr at 200 °C under pure H<sub>2</sub> of 20 mL min<sup>-1</sup>, followed by Ar purge with 20 mL min<sup>-1</sup> for 1 hr. For the *in-situ* DRIFT analysis of CO<sub>2</sub> adsorption, a CO<sub>2</sub> gas with a purity of 99.99 % was employed at a

flow rate of 20 mL min<sup>-1</sup>. For the *in-situ* DRIFT analysis of CO<sub>2</sub> methanation, a gas mixture of 20 mL min<sup>-1</sup> with 64 % H<sub>2</sub>, 16 % CO<sub>2</sub>, and 20 %  $N_2$  was introduced in the reaction cell.

Since CO is a key intermediate for  $CO_2$  methanation, the *in-situ* DRIFT analyses of CO adsorption and CO methanation have thus been conducted to better understand the mechanism. The adsorption of CO was investigated by using a 1.0 % CO/Ar gas at a flow rate of 20 mL min<sup>-1</sup> at 300 °C. After stabilizing for a while, argon was introduced to remove the physically adsorbed CO. The gas was then switched to 10 % H<sub>2</sub>/Ar in order to study the consumption of CO intermediates over time. For the *in-situ* DRIFT analysis of CO methanation, a gas mixture of 20 mL min<sup>-1</sup> with 4.0 % H<sub>2</sub>, 1.0 % CO, and 95 % Ar was introduced into the reaction cell.

# 2.3. $CO_2$ methanation

A fixed bed reactor was used to carry out  $CO_2$  methanation at atmospheric pressure. Quartz wool plugs were used to fix 50 mg fresh catalyst diluted with 200 mg silicon carbide. The catalyst was reduced at 200 °C for 1 hr by pure hydrogen (40 mL min<sup>-1</sup>). The feed gas was a mixture with the gas hourly space velocity (GHSV) of 60,000 mL·g<sup>-1</sup><sub>cat</sub>h<sup>-1</sup> and a stoichiometric feed ratio of H<sub>2</sub>/CO<sub>2</sub> (4/1), containing 16 % CO<sub>2</sub>, 64 % H<sub>2</sub>, and 20 % N<sub>2</sub>. The effluent was analyzed by an online gas



Fig. 2. HRTEM images and Ru particle size distribution of (a) 1 %Ru/DBD-ZrO<sub>2</sub> and (b) 1 %Ru/ZrO<sub>2</sub>; (c) HAADF-STEM image; (d) XRD patterns of 10 %Ru/DBD-ZrO<sub>2</sub> and (e) elemental mappings of 1 %Ru/DBD-ZrO<sub>2</sub> (Zr and Ru).

chromatograph (Agilent 6890D), equipped with a TCD and a Porapak Q column. CO<sub>2</sub> conversion ( $X_{CO2}$ ), CH<sub>4</sub> selectivity ( $S_{CH4}$ ), CH<sub>4</sub> yield ( $Y_{CH4}$ ), space-time yield (STY), the formation rate of CH<sub>4</sub> ( $R_{CH4}$ ), and turnover frequency (TOF) of CH<sub>4</sub> were calculated according to the following equations.

$$X_{\rm CO_2}(\%) = \frac{F_{\rm CO_2, in} - F_{\rm CO_2, out}}{F_{\rm CO_2, in}} \times 100\%$$
(1)

$$S_{\rm CH_4}(\%) = \frac{F_{\rm CH_4, out}}{F_{\rm CO_2, in} - F_{\rm CO_2, out}} \times 100\%$$
(2)

$$Y_{\rm CH_4}(\%) = \frac{F_{\rm CH_4, out}}{F_{\rm CO_2, in}} \times 100\%$$
(3)

$$STY = \frac{F_{CO_2, \text{ in }} \times X_{CO_2} \times S_{CH_4}}{m_{Ru}}$$
(4)

$$R_{\rm CH_4} = \frac{X_{\rm CO_2} \times S_{\rm CH_4} \times F_{\rm CO_2, \, in}}{W}$$
(5)

$$TOF = \frac{R_{CH_4} \times M_{Ru}}{D_{Ru}}$$
(6)

where  $F_{in}$  and  $F_{out}$  are the molar flow rates of CO<sub>2</sub> or CH<sub>4</sub> at the entrance and the exit of the reactor, respectively. *W* is the weight of the catalyst, while  $M_{Ru}$  and  $m_{Ru}$  are the molar mass and weight of Ru, respectively.  $D_{Ru}$  is the dispersion of the Ru catalyst.

The apparent activation energy of  $CO_2$  methanation was determined by the Arrhenius equation. The details for the calculation of the apparent activation energy have been described in our previous work [7].

# 3. Results and discussion

# 3.1. The enhanced hydrophilicity of zirconia

A significantly improved hydrophilicity of the ZrO<sub>2</sub> support was achieved by the DBD plasma treatment. As shown in Fig. 1(a,b), the instantaneous contact angle of water droplet on the surface of DBD-ZrO<sub>2</sub> and ZrO<sub>2</sub> is 11° and 49°, respectively. The infiltration of water droplet into the support only takes 0.68 s for DBD-ZrO<sub>2</sub>, while it needs 5.44 s for ZrO<sub>2</sub>. These indicate that the DBD plasma treated ZrO<sub>2</sub> has better hydrophilicity. As we know, the coverage of surface OH\* species plays an important role in the affinity of the material to water molecules [27]. More surface OH\* species lead to higher hydrophilicity [28]. From the UHV-FTIR spectra shown in Fig. 1(c), DBD-ZrO<sub>2</sub> exhibits a stronger OH\* peak at  $3450 \text{ cm}^{-1}$  than ZrO<sub>2</sub>. 1 %Ru/DBD-ZrO<sub>2</sub> also exhibits a stronger OH\* peak than 1 %Ru/ZrO2. This confirms that the enhanced hydrophilicity of DBD-ZrO<sub>2</sub> is caused by the increasing hydroxyl groups on the surface [29,30] from the DBD plasma treatment. The hydroxyl groups cannot only promote the chelation of metal ions but also have a strong affinity for Ru ions [31]. The rich hydroxyl groups can regulate the adsorption and diffusion of  $\mathrm{Ru}^{3+}$ , which is beneficial to the formation of uniformly dispersed Ru nanoparticles after the reduction by hydrogen [14,32]. The ZrO<sub>2</sub> support surface without plasma treatment has a low content of hydroxyl groups. The metal is easy to be agglomerated on the untreated support during the hydrogen reduction, causing the formation of larger Ru nanoparticles. This will be further discussed below.

Fig. 1(d) displays the XRD patterns of the catalysts and the corresponding supports. The individual  $ZrO_2$  support exhibits two major peaks at 2 $\theta$  of 28.22° and 31.49°, representing the diffraction of the (-111) and (111) facets of a monoclinic structure [33]. No Ru phase is observed in all samples. This indicates the high dispersion and small particle size of Ru species on  $ZrO_2$  [34,35]. It was reported that the highly dispersed Ru catalyst leads to not only a rapid dissociative adsorption of H<sub>2</sub> but also a hydrogen spillover [36]. Moreover, a shift of the  $ZrO_2$  peak to the lower angle is observed with the introduction of Ru.

# Table 1

Ru loading and dispersion of Ru/ZrO<sub>2</sub> catalysts and their TOF values based on  $\rm CO_2$  conversion.

Catalysts	Ru loading (wt%)	X <sub>CO2</sub> (%) (275 ℃)	S <sub>CH4</sub> (%) (275 ℃)	D <sub>Ru</sub> (%)	TOF (s <sup>-1</sup> )
1 %Ru/DBD- ZrO <sub>2</sub>	0.62	46.05	100	12.7	5.62
$1 \ \% Ru/ZrO_2$	0.65	21.10	100	9.0	3.44

This shift may be caused by the strong interaction between Ru and ZrO<sub>2</sub> [37]. Compared to 1 %Ru/ZrO<sub>2</sub>, a bigger shift of the ZrO<sub>2</sub> peak is observed over 1 %Ru/DBD-ZrO<sub>2</sub> (Fig. 1(d)). This means a stronger interaction exists on the 1 %Ru/DBD-ZrO<sub>2</sub> catalyst. Coincidentally, as shown in Figure S2, after the Ru loading, the Raman peaks of ZrO<sub>2</sub> are lower wavenumber-shifted and broadened, especially for 1 % Ru/DBD-ZrO<sub>2</sub>, due to the incorporation of Ru species in the ZrO<sub>2</sub> lattice. This is consistent with the result of XRD analyses [38]. For the DBD-ZrO<sub>2</sub> support, the Raman peak intensity reduces more significantly after the Ru loading. This may be caused by the increased light absorption due to the presence of more dispersed Ru on the surface of ZrO<sub>2</sub> [39]. Fig. 1(e, f) presents illustrative explanation of the effect of the ZrO<sub>2</sub> hydrophilicity on the preparation of the supported Ru catalysts.

The dispersion or the size of Ru catalyst on the support has a significant effect on the catalytic properties. As shown in Fig. 2(a, b), the TEM observations of the as-prepared catalysts reveal that the Ru particle size (3.20 nm) on the commercial ZrO2 (1 %Ru/ZrO2) is quite large, compared to that (1.77 nm) on the DBD plasma treated support (1 %Ru/ DBD-ZrO<sub>2</sub>). As shown in Table 1 and Figure S3, the metal dispersion of 1 %Ru/DBD-ZrO2 is 12.7 % by CO titration test, higher than that of 1 %  $Ru/ZrO_2$  (9.0 %). This confirms the previous speculation that the rich hydroxyl groups on the surface of the DBD treated ZrO<sub>2</sub> promote the capture and dispersion of Ru ions. Besides, the lattice spacing of Ru nanoparticles is 0.209 nm, corresponding well to the (101) crystal planes [40], which is further confirmed in the XRD patterns (Fig. 2(d)) by increasing the Ru loading to 10 wt%, while the diffraction peak at 44.00° is attributable to the (101) crystal plane of Ru [41]. The elemental mapping also shows that Ru is evenly distributed on the DBD treated ZrO<sub>2</sub> surface of 1 %Ru/DBD-ZrO<sub>2</sub> in Fig. 2(c, e). The surface area of 1 %Ru/DBD-ZrO<sub>2</sub> and 1 %Ru/ZrO<sub>2</sub> is 6.3 and 4.8 m<sup>2</sup> g<sup>-1</sup>, respectively, based on the BET measurements.

The XPS characterization was used to analyze the electronic structure of the samples before and after hydrophilicity modification. Firstly, ZrO<sub>2</sub> and DBD-ZrO<sub>2</sub> supports were analyzed by ex-situ XPS. As shown in Fig. 3(a, b), the O 1 s peak can be deconvoluted into three different components. The first one at 529.8 eV is ascribed to the lattice oxygen of ZrO<sub>2</sub> (O<sub>L</sub>), while the components at 531.4 and 532.6 eV are attributed to oxygen vacancy (Ov) and OH\* group, respectively [42,43]. The composition of  $O_v$  and  $OH^*$  group on DBD-ZrO<sub>2</sub> (28.9 % & 14.7 %) is about two times as large as ZrO<sub>2</sub> (16.3 % & 7.4 %). Similarly, ZrO<sub>2</sub> with partially reduced Zr species (Zr<sup>3+</sup>: 181.3, 183.2 eV) and stoichiometric Zr species (Zr<sup>4+</sup>: 182.1, 184.4 eV) [44,45] were recorded. DBD-ZrO<sub>2</sub> has a higher  $Zr^{3+}/(Zr^{3+}+Zr^{4+})$  ratio (12.3 %) than  $ZrO_2$  (5.5 %). This also indicates that DBD-ZrO<sub>2</sub> has more oxygen vacancies. The reasons are that the electrons, hydrated electrons, hydrogen radicals, and other active species within DBD plasma can cause reduction on the surface of the support [46,47]. This further confirms that the DBD plasma treatment facilitates the partial reduction of ZrO2 to create more oxygen vacancies.

Furthermore, the 1 %Ru/DBD-ZrO<sub>2</sub> and 1 %Ru/ZrO<sub>2</sub> catalysts were analyzed by *in-situ* XPS in Fig. 3(c, d). From Fig. 3(c), 1 %Ru/DBD-ZrO<sub>2</sub> has higher composition of O<sub>v</sub> (32.3 %) and OH\* (17.4 %) compared with 1 %Ru/ZrO<sub>2</sub> (27.9 % & 12.1 %) after hydrogen reduction. After introducing the feed gas at 350 °C for 90 min, the oxygen vacancies of both catalysts slightly increase. The hydroxyl groups decrease on 1 %Ru/ ZrO<sub>2</sub> more significantly than 1 %Ru/DBD-ZrO<sub>2</sub>. It has been known that



Fig. 3. The (a) O 1 s and (b) Zr 3d spectra of ZrO2 and DBD-ZrO2. The quasi in-situ XPS spectra of (c) O 1 s (d) Ru 3p of 1 %Ru/DBD-ZrO2 and 1 %Ru/ZrO2.

the oxygen vacancy is essential for CO<sub>2</sub> adsorption [48], while the surface OH\* species on the catalyst surface can directly participate in CO<sub>2</sub> hydrogenation through the addition of H atom of hydroxyl group into CO<sub>2</sub> [49]. With more oxygen vacancy and more OH\* species, 1 % Ru/DBD-ZrO<sub>2</sub> is thus more beneficial to the activation of CO<sub>2</sub> and subsequent hydrogenation to methane.

In Fig. 3(d), the 3p peak of Ru was split into two peaks. Peaks observed at 460.8 and 483.1 eV are attributed to Ru<sup>0</sup> 3p<sub>3/2</sub> and 3p<sub>1/2</sub>, respectively[50,51]. Additionally, peaks at 461.7 and 484.0 eV are assigned to Ru<sup> $\delta$ +</sup> 3p<sub>3/2</sub> and 3p<sub>1/2</sub>, respectively. After hydrogen reduction, the composition of Ru<sup> $\delta$ +</sup> in the 1 %Ru/DBD-ZrO<sub>2</sub> (48.1 %) is higher than that in the 1 %Ru/ZrO<sub>2</sub> (38.9 %), this suggests that more Ru species of 1 %Ru/DBD-ZrO<sub>2</sub> are in some positively charged status. As reported in the literature [23,52,53], there exists a strong electronic metal-support interaction, causing a charge transfer from the Ru nanoparticle to the adjacent oxygen vacancy in the ZrO<sub>x</sub> surface and making the Ru species be positively charged as Ru<sup> $\delta$ +</sup>. This further leads to

stronger Ru-CO bonding and enhanced methanation of adsorbed CO\*, as confirmed below. Besides, the contents of metallic Ru<sup>0</sup> or Ru<sup> $\delta$ +</sup> species of the two catalysts remain almost unchanged during the reaction process. No new Ru species can be observed. This indicates that the metallic Ru species have not been oxidized by the *in-situ* generated H<sub>2</sub>O.

Fig. 4(a) shows the H<sub>2</sub>-TPR profiles of the catalysts before hydrogen reduction. Three regions can be observed for 1 %Ru/DBD-ZrO<sub>2</sub> and 1 % Ru/ZrO<sub>2</sub>. According to the literature, the peaks in the TPR profile of Ru/ZrO<sub>2</sub> catalysts are due to the reduction of ruthenium oxides with different particle sizes or different metal-support interaction strength [54,55]. The low-temperature reduction peaks likely correspond to the weak interaction between the large-size metal nanoparticle and the support or the reduction of ruthenium oxide species with smaller particles, while the larger ruthenium oxide particle or the small-size Ru particle of strong interaction with the support is reduced at high temperatures [56,57]. The 1 %Ru/DBD-ZrO<sub>2</sub> catalyst has been proven to have a smaller Ru size. Therefore, for 1 %Ru/DBD-ZrO<sub>2</sub>, the reduction



Fig. 4. (a) H2-TPR profiles of 1 %Ru/DBD-ZrO2 and 1 %Ru/ZrO2 before hydrogen reduction. (b) H2-D2 exchange experiment of Normalized HD formation rate over 1 %Ru/DBD-ZrO<sub>2</sub>, 1 %Ru/ZrO<sub>2</sub>, DBD-ZrO<sub>2</sub> and ZrO<sub>2</sub>. (c, d) H<sub>2</sub>-TPD-MS profiles of ZrO<sub>2</sub> and DBD-ZrO<sub>2</sub> supports. (H<sub>2</sub>: m/z=2; H<sub>2</sub>O: m/z=18). (e) CO<sub>2</sub>-TPD curves of 1 %Ru/DBD-ZrO2 and 1 %Ru/ZrO2. Schematic representation of Ru particles, oxygen vacancy, and OH\* groups on the surface of (f) 1 %Ru/DBD-ZrO2 and (g) 1 % Ru/ZrO2 catalysts.

temperature of Ru species at  ${\sim}112~^\circ\text{C}$  is higher than that of 1 %Ru/ZrO<sub>2</sub> (~83 °C). This indicates that 1 %Ru/DBD-ZrO $_2$  has a stronger interaction between Ru and the support. It has been reported that the supported Ru catalyst of strong electronic interaction with the support is responsible for readily breaking the C-O bonds of CO<sub>2</sub> [58,59] and the presence of Zr-O-Ru interfacial sites would accelerate CO dissociation [60,61].

The peaks at  ${\sim}383$  °C can be assigned to the surface reduction of the support [62]. The peak at a higher temperature of 449 °C represents the reduction of ZrO<sub>2</sub> at the Ru-ZrO<sub>2</sub> interface by hydrogen spillover [63, 64]. This will lead to further generation of oxygen vacancies. The effect of oxygen vacancies on hydrogen dissociation will be discussed below.

The H<sub>2</sub> dissociation and subsequent hydrogenation play a pivotal



Fig. 5. (a)  $CO_2$  methanation conversion, selectivity, and equilibrium conversion and (b) yield on 1 %Ru/DBD-ZrO<sub>2</sub> and 1 %Ru/ZrO<sub>2</sub> catalysts. (c) Comparison of activity of DBD-ZrO<sub>2</sub> loading with different content of Ru. (d) Arrhenius plot for  $CO_2$  methanation in the temperature range between 240 °C and 270 °C for both 1 % Ru/DBD-ZrO<sub>2</sub> and 1 %Ru/ZrO<sub>2</sub> catalysts.

role in selective hydrogenation. The ability of  $H_2$  dissociation over different catalysts and supports was investigated by  $H_2$ - $D_2$  exchange of  $H_2$  and  $D_2$  in Fig. 4(b). The normalized HD intensity of 1 %Ru/DBD-ZrO<sub>2</sub> is higher than 1 %Ru/ZrO<sub>2</sub>, suggesting that 1 %Ru/DBD-ZrO<sub>2</sub> catalyst has stronger  $H_2$  dissociation ability. This is because 1 %Ru/DBD-ZrO<sub>2</sub> has highly dispersed Ru particles and strong electron interactions between the Ru and DBD-ZrO<sub>2</sub> [60,65]. The normalized HD intensity of DBD-ZrO<sub>2</sub> is 2.4 times higher than ZrO<sub>2</sub>, this suggests that oxygen vacancy on the DBD surface can also promote the activation and dissociation of  $H_2$ .

The H<sub>2</sub>-TPD-MS on ZrO<sub>2</sub> and DBD-ZrO<sub>2</sub> supports were performed respectively to further investigate the effect of oxygen vacancies on hydrogen adsorption and activation. As shown in Fig. 4(c, d), compared to ZrO<sub>2</sub>, the peaks at 247 °C on H<sub>2</sub>-TPD-MS curves of DBD-ZrO<sub>2</sub> can be assigned to the desorption of middle-intensive H<sub>2</sub> adsorption, which plays the most important role in the activation of H<sub>2</sub> molecules [66,67]. And, DBD-ZrO<sub>2</sub> shows a significant increase in the amount of H<sub>2</sub> adsorption sites at 336 °C, corresponding to the CO<sub>2</sub> methanation reaction, which mostly occurs at the temperature of 200–375 °C. Moreover, the H<sub>2</sub>O signal is detected during the degassing process of both supports, while DBD-ZrO<sub>2</sub> exhibits a higher H<sub>2</sub>O peak at both low and high temperatures. These indicate that DBD-ZrO<sub>2</sub> with more oxygen vacancies has better hydrogen dissociation ability.

The CO<sub>2</sub>-TPD was tested to understand the obvious differences in the activities of the 1 %Ru/ZrO<sub>2</sub> and 1 %Ru/DBD-ZrO<sub>2</sub> catalysts (Fig. 4(e)). The desorption curves of the catalysts can be divided into three zones located in the temperature range of <150 °C, 150–400 °C and >400 °C, assigned to the weak (molecularly adsorbed CO<sub>2</sub>), medium-strength (HCO<sub>3</sub> or HCO<sub>2</sub>), and strong basic sites (bidentate carbonates (b-CO<sub>3</sub><sup>2-</sup>)) and monodentate carbonates (m-CO<sub>3</sub><sup>2-</sup>)), respectively [68,69]. It has been reported that the medium-strength basic sites are essential for the

adsorption and decomposition of  $CO_2$  [70]. The integral area of the zone follows as 1 %Ru/DBD-ZrO<sub>2</sub>>1 %Ru/ZrO<sub>2</sub> in the temperature range of 150–400 °C. This suggests that 1 %Ru/DBD-ZrO<sub>2</sub> has a larger number of medium-strength basic sites. According to the XRD, Raman, XPS, H<sub>2</sub>-TPR, and CO<sub>2</sub>-TPD results, as shown in Fig. 4(f, g), 1 %Ru/DBD-ZrO<sub>2</sub> has more OH\* groups, more oxygen vacancies, stronger electronic metal support interaction and smaller Ru nanoparticles. All these lead to improved CO<sub>2</sub> adsorption-decomposition and H<sub>2</sub> dissociation, resulting in the superior performance of the 1 %Ru/DBD-ZrO<sub>2</sub> catalyst.

In addition, the average diameter of Ru nanoparticles remains almost unchanged after the reaction for 1 %Ru/DBD-ZrO<sub>2</sub>, with a value of 1.77 nm before and 1.79 nm after the reaction, as shown in Fig. 2(a) and S4(a). However, the 1 %Ru/ZrO<sub>2</sub> catalyst shows an obvious aggregation, as exhibited in Fig. 2(b) and S4(b). This indicates that the support with enhanced hydrophilicity can better stabilize Ru nanoparticles during the reaction process and prevent them from aggregation. This also corresponds to the stability test results. 1 %Ru/DBD-ZrO<sub>2</sub> well maintains its initial activity, while the activity of 1 %Ru/ZrO<sub>2</sub> reduces slightly in the first 10 minutes (Figure S5).

# 3.2. The catalytic activity

In Fig. 5(a, b), the overall activity of  $1 \,\%$ Ru/DBD-ZrO<sub>2</sub> is significantly higher than  $1 \,\%$ Ru/ZrO<sub>2</sub>, especially at low reaction temperatures. For example,  $\sim 10 \,\%$  CO<sub>2</sub> conversion is achieved at 225 °C and 250 °C on  $1 \,\%$ Ru/DBD-ZrO<sub>2</sub> and  $1 \,\%$ Ru/ZrO<sub>2</sub>, respectively. Besides, at 275 °C, the CO<sub>2</sub> conversion and CH<sub>4</sub> yield of  $1 \,\%$ Ru/DBD-ZrO<sub>2</sub> all reach 46.2 %, which are twice higher than that of  $1 \,\%$ Ru/ZrO<sub>2</sub> ( $\sim 21.1 \,\%$ ). Based on the Ru dispersion measured by CO titration test and the Ru loading measured by ICP, the TOF values towards CH<sub>4</sub> at 275 °C have been calculated in Table 1. Apparently,  $1 \,\%$ Ru/DBD-ZrO<sub>2</sub> shows a higher TOF



Fig. 6. In-situ DRIFT spectra during (a, b) CO<sub>2</sub> adsorption (99.99 % CO<sub>2</sub>) and (c, d) CO<sub>2</sub> methanation (64 % H<sub>2</sub>, 16 % CO<sub>2</sub> and 20 % N<sub>2</sub>) over 1 %Ru/ZrO<sub>2</sub> and 1 % Ru/DBD-ZrO<sub>2</sub> at a flow rate of 20 mL min<sup>-1</sup> with a heating rate of 10 °C min<sup>-1</sup>.

(5.62 s<sup>-1</sup>>3.44 s<sup>-1</sup>). These results indicate the significantly improved low-temperature activity of 1 %Ru/DBD-ZrO<sub>2</sub>. Moreover, 100 % CH<sub>4</sub> selectivity is achieved on both catalysts under 300 °C. The selectivity of CO at temperatures above 300 °C (up to 375 °C) is only less than 3 % for 1 %Ru/DBD-ZrO<sub>2</sub> catalysts. At 350 °C, the STY of CH<sub>4</sub> for 1 %Ru/DBD-ZrO<sub>2</sub> reaches the maximum value of 52.97 mol  $g_{Ru}^{-1}$  h<sup>-1</sup> (0.33 mol  $g_{cat}^{-1}$  h<sup>-1</sup>), higher than 1 %Ru/ZrO<sub>2</sub> and the other catalysts reported in the literature (Table S1).

The effect of the Ru loading was also investigated. As exhibited in Fig. 5(c), 1 %Ru/DBD-ZrO<sub>2</sub> possesses the best Ru atom utilization for CO<sub>2</sub> methanation among the Ru/DBD-ZrO<sub>2</sub> catalysts tested with the Ru loading of 0.5 %, 1 % and 2 %. There exists an optimum Ru loading that is 1 %. The stability tests were then performed on both 1 %Ru/DBD-ZrO<sub>2</sub> and 1 %Ru/ZrO<sub>2</sub> at a GHSV of 60,000 mL·g<sub>cat</sub>h<sup>-1</sup> under 300 °C. As shown in Figure S5, the stable catalytic activities can be well maintained for 480 minutes over 1 %Ru/DBD-ZrO<sub>2</sub>. However, there is a slight decrease in activity within the initial 10 minutes over 1 %Ru/ZrO<sub>2</sub>. Kinetic studies have been further carried out to compare the kinetic parameters of 1 %Ru/DBD-ZrO<sub>2</sub> and 1 %Ru/ZrO<sub>2</sub> (83.44 kJ/mol) is less than 1 %Ru/ZrO<sub>2</sub> (98.78 kJ/mol). The former catalyst is more active than the latter under the same reaction conditions.

#### 3.3. The reaction mechanism

The plasma treatment can effectively improve the hydrophilicity of

the support and promote better dispersion of Ru to form smaller Ru nanoparticles, causing the significantly improved activity. To understand the mechanism of CO<sub>2</sub> methanation reaction, the *in-situ* DRIFT analyses were carried out over  $1 \,$ %Ru/ZrO<sub>2</sub> and  $1 \,$ %Ru/DBD-ZrO<sub>2</sub>.

The in-situ DRIFT analyses of CO2 adsorption were firstly conducted. As shown in Fig. 6(a, b), for 1 %Ru/ZrO<sub>2</sub>, with the slightly decreasing bands of  $HCO_3^*$  (1618, 1423, 1213 cm<sup>-1</sup>) [37], the bands of bri-CO-interface (1900–1860 cm<sup>-1</sup>) [15,71] begin to increase at 150 °C and then slightly reduce at 350 °C. For 1 %Ru/DBD-ZrO2, HCO3\* is almost completely consumed as the elevated temperature, while the bands of bri-CO-interface rapidly increase before 300 °C and then sharply disappear at 350 °C. Meanwhile, the peak of hydroxyl groups gradually decreases with increasing temperature. These suggest that CO<sub>2</sub> is more easily to be converted into HCO<sub>3</sub>\* by combining with OH\* (terminal hydroxyls ( $OH_T^*$ : 3730 cm<sup>-1</sup>) and bridging hydroxyls ( $OH_B^*$ : 3700-3595 cm<sup>-1</sup>) [30,72,73]). HCO<sub>3</sub>\* is then dissociated into bri-CO species over 1 %Ru/DBD-ZrO2. After that, further reactions occur. The production of more HCO<sub>3</sub>\* indirectly reflects the presence of more OH\* on the 1 %Ru/DBD-ZrO<sub>2</sub> surface, which can combine with CO<sub>2</sub>. What's more, the intensity of  $m-CO_3^{2-}$  bands (1508 and 1335 cm<sup>-1</sup>) [37,71] for 1 %Ru/DBD-ZrO<sub>2</sub> is much stronger than that for 1 %Ru/ZrO<sub>2</sub>. This indicates that 1 %Ru/DBD-ZrO<sub>2</sub> has a stronger ability to adsorb CO<sub>2</sub>. This is due to the fact that 1 %Ru/DBD-ZrO2 possesses more oxygen vacancies. The consumption of OH\* groups in 1 %Ru/DBD-ZrO2 is also greater than that in 1 %Ru/ZrO<sub>2</sub> from 50 to 100  $^{\circ}$ C, indicating that 1 % Ru/DBD-ZrO<sub>2</sub> has more OH\* groups involved in the reaction, which combines with  $CO_2$  to form  $HCO_3^*$ .



**Fig. 7.** *In-situ* DRIFT spectra during CO methanation (4.0 % H<sub>2</sub>, 1.0 % CO, and 95 % Ar) over (a)  $1 \, \%$ Ru/DBD-ZrO<sub>2</sub> and (b)  $1 \, \%$ Ru/ZrO<sub>2</sub> at a flow rate of 20 mL min<sup>-1</sup> with a heating rate of 10 °C min<sup>-1</sup>. (c) The *in-situ* DRIFT spectra in 1 % CO/Ar and then in 10 % H<sub>2</sub>/Ar on 1 % Ru/DBD-ZrO<sub>2</sub> at 300 °C.

To explore the evolution of the surface species of CO<sub>2</sub> methanation, the *in-situ* DRIFT spectra were recorded at 50–350 °C with a gas mixture of 64 % H<sub>2</sub>, 16 % CO<sub>2</sub> and 20 % N<sub>2</sub>. As shown in Fig. 6(c, d), some new bands appear in comparison with the *in-situ* DRIFT spectra of CO<sub>2</sub> adsorption. The bands of  $CH_4$ \* at 1302 and 3014 cm<sup>-1</sup> present with the bands of CH<sub>3</sub>\* (2958 cm<sup>-1</sup>) and HCOO\* (1577 cm<sup>-1</sup>) [74,75]. For both catalysts, with the disappearance of the bands of HCO<sub>3</sub>\* at 150 °C, the bands of HCOO\* appear at 150 °C and reach the maximum intensity at 200 °C. The intensity of these bands then reduces until they disappear at 350 °C. At the same time, the CH<sub>4</sub>\* bands appear at 200 °C and increase with the increasing temperatures. This indicates that HCO3\* is converted to HCOO\* and then converted to CH<sub>3</sub>\* and further to CH<sub>4</sub>, which suggests that the formate pathway exists in both catalysts. It is noteworthy that the bands intensity of HCO<sub>3</sub>\* of 1 %Ru/DBD-ZrO<sub>2</sub> is higher than that of 1 %Ru/ZrO<sub>2</sub> in the *in-situ* DRIFT spectra of CO<sub>2</sub> adsorption. However, the strength of HCOO\* bands of the two catalysts is almost the same in the in-situ DRIFT spectra of CO2 methanation. This indicates that 1 %Ru/DBD-ZrO2 promotes the conversion of HCO3\* to HCOO\*, enhancing the formate pathway. Moreover, in Fig. 6(c, d), for 1 % Ru/DBD-ZrO2 catalyst, the OH\* groups decrease gradually with the increase of temperature before 300 °C, and it almost remains unchanged after 300 °C. For 1 % Ru/ZrO2 catalyst, the OH\* group is gradually consumed with increasing temperature. Especially at 350 °C, there is a significant consumption of OH\* groups compared to 300 °C. This is because, when the reaction temperature reaches 300 °C, H<sub>2</sub>O molecules are more easily adsorbed on the hydrophilic 1 %Ru/DBD-ZrO2 catalyst [15], then dissociate to OH\*, which increases the concentration of OH\* and enhances the opportunity for high concentration OH\* groups to

combine with  $CO_2$  to generate  $HCO_3^*$ .  $HCO_3^*$  will be then converted to  $HCOO^*$ . These indicate that  $H_2O$  molecules are involved in the reaction and the improvement of hydrophilicity is beneficial to the enhancement of formate pathway.

Moreover, 1 %Ru/DBD-ZrO<sub>2</sub> has a higher proportion of CO<sup>\*</sup> adsorption, compared with 1 %Ru/ZrO<sub>2</sub>. To explore the conversion of CO<sup>\*</sup> intermediate to CH<sub>4</sub>\*, the *in-situ* DRIFT analyses of CO methanation were also conducted with a gas mixture of 4.0 % H<sub>2</sub>, 1.0 % CO, and 95 % Ar. As shown in Fig. 7(a, b), the CH<sub>2</sub>\* (2851 cm<sup>-1</sup>), CH<sub>3</sub>\*(2958 cm<sup>-1</sup>) and CH<sub>4</sub>\* (3014 cm<sup>-1</sup>) bands [71,76–78] appear at 100 °C over 1 % Ru/DBD-ZrO<sub>2</sub>, while these bands only start to present at 300 °C for 1 % Ru/DBD-ZrO<sub>2</sub> catalyst promote the breaking of C-O bonds, accelerate the conversion of CO, and facilitate the CO pathway. In addition, there exist different modes of CO adsorption, and 1 %Ru/DBD-ZrO<sub>2</sub> has a greater linear-CO-Ru<sup>0</sup> (2070–1995 cm<sup>-1</sup>) [15,71] adsorption capacity than 1 %Ru/ZrO<sub>2</sub>.

In order to investigate the effect of the CO adsorption mode, the *in*situ DRIFT analyses were conducted at 300 °C. Firstly, when the inlet gas is 1 % CO/Ar, the CO\* intermediate reaches stability within 5 minutes. The linear-CO-Ru<sup>0</sup> and bri-CO-interface bands co-exist on the catalyst surface, as shown in Fig. 7(c). After purging with Ar for two minutes to remove the physically adsorbed CO, the feed gas is switched to 10 % H<sub>2</sub>/ Ar. Both bands of linear-CO-Ru<sup>0</sup> and bri-CO-interface adsorption reduce until they disappear after around 5 min. With the disappearance of CO\* bands, HCOO\*, m-CO<sub>3</sub><sup>2-</sup> and CH<sub>4</sub>\* bands appear immediately. Then HCOO\* and m-CO<sub>3</sub><sup>2-</sup> bands disappear after 3 min. This indicates that both linear and bridged adsorbed CO\* can be hydrogenated to produce



Fig. 8. Proposed pathways for CO<sub>2</sub> methanation over 1 %Ru/ZrO<sub>2</sub> and 1 %Ru/DBD-ZrO<sub>2</sub> catalysts. (The adsorption form of hydroxyl is exemplified by the terminal hydroxyl configuration.).

 $CH_4^*$ . All these are caused by the high dispersion and small Ru nanoparticles on the hydrophilic  $ZrO_2$  surface. According to the discussions above,  $CO_2$  methanation can occur on both catalysts through  $CO^*$ pathway, while 1 %Ru/DBD-ZrO<sub>2</sub> can promote  $CO^*$  pathway by the enhanced adsorption of linear-CO-Ru<sup>0</sup>.

In summary, the *in-situ* DRIFT spectra analyses confirm that the formate pathway and CO<sup>\*</sup> pathway co-exist for CO<sub>2</sub> methanation on 1 % Ru/ZrO<sub>2</sub> and 1 %Ru/DBD-ZrO<sub>2</sub>. For the formate pathway, as shown in the left side of Fig. 8, CO<sub>2</sub> interacts with surface OH<sup>\*</sup> to produce adsorbed HCO<sub>3</sub><sup>\*</sup>, which is further converted into HCOO<sup>\*</sup>, followed by the formation of CH<sub>4</sub><sup>\*</sup>. This reaction pathway is enhanced by the abundant hydroxyl groups on the catalyst surface. Highly dispersed Ru particles formed on the surface of hydrophilic support can provide more linear-CO-Ru<sup>0</sup> adsorption on 1 %Ru/DBD-ZrO<sub>2</sub>, as shown in the right side of Fig. 8. The CO<sub>2</sub> adsorbed is firstly converted into CO<sup>\*</sup> through HCO<sub>3</sub><sup>\*</sup> or direct dissociation CO<sub>2</sub>, followed by the hydrogenation to CH<sub>4</sub> through linear-CO-Ru<sup>0</sup> adsorption.

# 4. Conclusion

In this work, we confirmed that the hydrophilicity of zirconia has significant effect on the properties of the Ru/ZrO2 catalyst for CO2 methanation. A rapid and convenient DBD plasma treatment has been demonstrated to be effective to enhance the hydrophilicity of zirconia. The Ru catalyst was further prepared using the conventional wet impregnation, chemical pre-reduction and the hydrogen reduction with the plasma treated  $ZrO_2$  as the support. The DBD plasma treated  $ZrO_2$ (DBD-ZrO<sub>2</sub>) possesses more surface oxygen vacancies and OH\* groups than the un-treated ZrO<sub>2</sub> support. Compared to the Ru catalyst on the un-treated ZrO<sub>2</sub>, the enhanced hydrophilicity of zirconia leads to highly dispersed Ru catalyst with smaller size (1.77 vs. 3.20 nm) and stronger electronic interaction between Ru and the support, which forms the plentiful interfacial active sites and facilitates the adsorptiondecomposition of CO2 and dissociation of H2. The Ru catalyst supported by the plasma treated ZrO<sub>2</sub> (Ru/DBD-ZrO<sub>2</sub>) shows a significantly improved activity for CO<sub>2</sub> methanation. At the same CO<sub>2</sub> conversions, the reaction temperature over Ru/DBD-ZrO2 with 1 wt% Ru loading is

20–70 °C lower than the Ru catalyst on the un-treated  $ZrO_2$ . The *in-situ* DRIFT analyses show that  $CO_2$  methanation follows both the formate pathway and CO\* pathway on Ru/DBD-ZrO<sub>2</sub> and Ru/ZrO<sub>2</sub>. For the formate pathway,  $CO_2$  interacts with surface OH\* to produce adsorbed HCO<sub>3</sub>\*, which is further converted to HCOO\*, followed by the formation of CH<sub>4</sub>\*. The enhanced CO<sub>2</sub> adsorption and the consumption of HCO<sub>3</sub>\* and HCOO\* are observed over the Ru/DBD-ZrO<sub>2</sub> catalyst, which facilitates the formate pathway. For the CO\* pathway, CO\* is formed via the conversion of the adsorbed CO<sub>2</sub> through HCO<sub>3</sub>\* or via the direct decomposition of CO<sub>2</sub>, followed by the hydrogenation to CH<sub>4</sub>. The Ru/DBD-ZrO<sub>2</sub> catalyst begins to show stronger linear-CO-Ru<sup>0</sup> adsorption, which favors the CO\* pathway. Consequently, both the formate pathway and CO\* pathway are enhanced over the Ru/DBD-ZrO<sub>2</sub> catalyst.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data Availability

Data will be made available on request.

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# Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2024.124549.

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