PdCu supported on dendritic mesoporous $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ as superior catalysts to boost CO_2 hydrogenation to methanol

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ABSTRACT

A dendritic PdCu/Ce_{0.3}Zr_{0.7}O₂ (PdCu/CZ-3) catalyst with uniform spherical morphology was prepared for boosting the catalytic performance of CO₂ hydrogenation to methanol (MeOH). The open dendritic pore channels and small particle sizes could reduce not only the diffuse resistance of reactants and products but also increase the accessibility between the active sites (PdCu and oxygen vacancy) and the reactants (H₂ and CO₂). More spillover hydrogen could be generated due to the highly dispersed PdCu active metals over the PdCu/CZ-3 catalyst. PdCu/CZ-3 can stimulate the generation of more Ce³⁺ cations, which is beneficial to produce more oxygen vacancies on the surface of the CZ-3 composite. Spillover hydrogen and oxygen vacancy could promote the formate and methoxy routes over PdCu/CZ-3, the

primary intermediates producing MeOH. PdCu/CZ-3 displayed the highest CO₂ conversions (25.5 %), highest MeOH yield (6.4 %), highest PdCu-TOF_{MeOH} (7.7 h⁻¹) and superior 100 h long-term stability than those of other PdCu/Ce_xZr_{1-x}O₂ analogs and the reference PdCu/CeO₂ and PdCu/ZrO₂ catalysts. Density functional theory (DFT) calculations and in situ DRIFTS were performed to investigate the CO₂-MeOH hydrogenation mechanism.

KEYWORDS

Dendritic PdCu/Ce_{0.3}Zr_{0.7}O₂ catalyst, Hydrogen spillover, Oxygen vacancy, CO₂ hydrogenation, methanol

1. INTRODUCTION

The efficient use of CO₂ has attracted increasing attention due to the concerns raised by unrestricted CO₂ emissions [1-5]. It is challenging to convert CO₂ because of its high thermodynamic stability [6]. However, the conversion of CO₂ is feasible when molecular hydrogen (H₂) with a high Gibbs free energy is used as the reductant [7]. Hydrogenation of CO₂ to produce sustainable chemical feedstocks and fuels is one of the promising methods for CO₂ utilization using green H₂ [8-13]. CO₂ hydrogenation can lead to the production of a wide range of compounds, including liquid fuels, lower olefins, and aromatics [14-16]. Among them, MeOH has been extensively studied because it can be used as a fuel directly and as essential raw material to prepare other chemical products [17-20].

Cu-based catalysts are widely studied among MeOH synthesis catalysts due to their low cost compared with Au- and Pt-based catalysts [21]. However, Cu-based catalysts are not as effective in the low-temperature hydrogenation reactions as Pd-based catalysts [22, 23]. Song et al. recently reported that PdCu supported on silica showed a better performance of CO₂ hydrogenation than the monometallic catalysts [24]. Density functional theory calculations also suggested that PdCu catalysts favor the surface CO₂ hydrogenation to formate (HCOO*), a key intermediate in the

mechanism of methanol formation [25]. A series of oxide supports, such as CeO_2 , TiO_2 , SiO_2 , ZrO_2 , Al_2O_3 , have been studied for CO_2 hydrogenation reactions [26-32]. Among these oxide supports, CeO_2 is one of the most critical components in CO_2 hydrogenation catalysts because of its superior redox characteristics and many oxygen vacancies. Moreover, Ce atoms in the CeO_2 crystal can be replaced by Zr atoms to form $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions, promoting the generation of more oxygen vacancies and thermal stability of CeO_2 [33, 34]. Our previous work [35, 36] demonstrated that dendritic catalysts with open-pore channels could easily enable the reactants and products to enter into and out of their pores with lower diffusion resistance to access the active phases. However, the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution with dendritic morphology has never been reported. Hence, the design and preparation of dendritic $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ supported PdCu catalysts with open pore channels, and superior accessibility between catalyst and reactants is desirable for improving the MeOH formation from CO_2 hydrogenation.

In this study, the dendritic $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution was successfully prepared via the solvent evaporation-induced self-assembly (EISA) method using dendritic mesoporous silica nanoparticles (DMSNs) as the hard template. Pure CeO_2 and ZrO_2 materials were also prepared as reference supports. The corresponding multifunctional catalysts PdCu/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ and the reference catalysts PdCu/ CeO_2 and PdCu/ ZrO_2 were synthesized using the co-impregnation method. The PdCu/ $\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalyst with good dendritic morphology exhibited the highest CO_2 conversions (25.5 %), MeOH yield (5.8 %), and superior 100 h long-term stability compared with those of other PdCu/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts and the reference PdCu/ CeO_2 and PdCu/ ZrO_2 catalysts. The best CO_2 hydrogenation activity of PdCu/ $\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalyst can be ascribed to its relative open-pore channels, small particle sizes, higher metal dispersion, better hydrogen dissociation capability, and a more significant number of oxygen vacancies. Moreover, the CO_2 hydrogenation mechanism was studied by in situ DRIFTS and DFT calculations.

2. EXPERIMENTAL

2.1 Synthesis of dendritic $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions

2.1.1 Synthesis of DMSNs hard template

Preparation of DMSNs hard templates were described in our previous work [37]. Source and purity of all chemicals used in this work were specified in Table S1 (Supporting Information).

2.1.2 Synthesis of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$.

Dendritic $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions were prepared via EISA method using DMSNs as the hard template with the assistance of acetone solvent. 12 mmol (5.21 g) of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0, 1.66, 3.87, 9.02 g) with various Ce/Zr molar ratios (1:0, 7:3, 5:5, 3:7) was dissolved into 15.0 mL of acetone. Moreover, 9.02 g of single $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was also dissolved into 15.0 mL of acetone. After the solution was rapidly stirred to clear, 2.0 g of DMSNs was added, and then ultrasonic dispersion was carried out for 5 min. The mixture was stirred at 30 °C for another two hours before it was transferred to the oven where it was dried at 80 °C for 12 hours. The resulting solid powder was calcined in air at 500 °C with a heating rate of 1 °C min^{-1} for 4 hours to decompose the precursors. Finally, 100.0 mL of 2.0 M NaOH aqueous solution was added to the resulting samples and stirred for 1 hour to eliminate the DMSNs template. This process was repeated three times. The obtained $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions with various Ce/Zr molar ratios (1:0, 7:3, 5:5, 3:7, 0:1) were labelled as CeO_2 , CZ-1, CZ-2, CZ-3 and ZrO_2 , respectively.

2.2 Preparation of the corresponding catalysts.

Dendritic $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution supported PdCu bimetallic catalysts were prepared by incipient wetness co-impregnation method using acetone solution of $\text{Pd}(\text{CH}_3\text{COO})_2$ (Aldrich, >98 wt.%) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich, ≥ 98 wt.%). The impregnated samples were dried at 80 °C for 12 hours and calcined in an electric furnace at 450 °C for 5 hours. Pd and Cu metal loadings were 5.7 wt. % and 10 wt. %, respectively. The actual Pd and Cu metal loadings were determined by inductive coupled plasma optical emission spectrometry (ICP-OES) analysis and the

corresponding data was summarized in Table S3 (Supporting Information). The corresponding PdCu/Ce_xZr_{1-x}O₂ catalysts with different Ce/Zr molar ratios (1:0, 7:3, 5:5, 3:7, 0:1) were labelled as PdCu/CeO₂, PdCu/CZ-1, PdCu/CZ-2, PdCu/CZ-3 and PdCu/ZrO₂, respectively.

2.3 CO₂ hydrogenation evaluation and DFT computation

The catalysts were tested using a feed gas of CO₂/H₂ (25/75, vol %) in a 16 channel Flowrence from Avantium consisting of 16 stainless steel tubes with an internal diameter of 2 mm and 30cm length placed in a furnace. One of the reactors was used empty as a blank. Moreover, 0.5 mL/min of He was added to the mixture as the internal standard. Before the CO₂ hydrogenation, 50 mg of each catalyst (150 μm–250 μm) was pretreated under an H₂ atmosphere at 300 °C for 2 hours. After H₂ pretreatment, the reaction tubes were cooled to room temperature. The reaction system was then pressurized to 5.0 MPa with a mixture of CO₂/H₂/He gas. The standard reaction conditions were 250 °C, 5.0 MPa with a gas hourly space velocity (GHSV) of 3600 mL g_{cat}⁻¹ h⁻¹ (STP). The products were analyzed by an online Agilent 7890B gas chromatograph (GC) equipped with a TCD and 2 FIDs. One loop was used to detect He, CO₂ and CO (Column HaysepQ6 Ft G3591-80013, TCD), while another one was used for CH₃OH (Column Innowax 45 m, 0.2 mm OD, front FID) and CH₄ (Column Gaspro 30M, 0.32 mm OD, back FID). The CO₂ conversions (X_{CO₂}, %) and MeOH yields (Y_{MeOH}, %) are calculated by the following formula:

$$X_{CO_2} = \left(1 - \frac{C_{He, B} \cdot C_{CO_2, R}}{C_{He, R} \cdot C_{CO_2, B}} \right) \cdot 100$$

$$Y_{MeOH} = \frac{\left(\frac{C_{MeOH, R}}{C_{He, R}} \right)}{\left(\frac{C_{CO_2, B}}{C_{He, B}} - \frac{C_{CO_2, R}}{C_{He, R}} \right)} \cdot X_{CO_2}$$

where C_{He,B}, C_{CO₂,B}, C_{CO₂,R} and C_{He,R} represent the concentrations of He of blank reactor, CO₂ of blank reactor, CO₂ of the products and He of the products, respectively; C_{MeOH, R} represent the MeOH concentration analyzed by GC. Carbon

balance closure was better than 99% in all cases.

The DFT computational method and periodic models (Fig. S5) are displayed in the Supporting Information.

2.4 Characterization and catalytic evaluation

X-ray diffraction measurements (XRD) were carried out using a Bruker D8 diffractometer. Nitrogen adsorption-desorption isotherms were obtained by a Micromeritics ASAP 2040 at $-196\text{ }^{\circ}\text{C}$. Before the experiments, samples and catalysts were degassed at $150\text{ }^{\circ}\text{C}$ for 10 hours. Temperature-programmed reduction (TPR) experiments with H_2 were performed using a Micromeritics Autochem 2920 setup. Before the reduction, the catalysts were pretreated at $350\text{ }^{\circ}\text{C}$ for 4 hours using argon gas, and then the temperature was lowered to $50\text{ }^{\circ}\text{C}$. Temperature-programmed desorption (TPD) measurements with H_2 and CO_2 were carried out using Altamira Instruments AMI-200 IP equipment. Scanning electron microscopy (SEM) images were collected on a FEI TENE0 VS microscope. The Pd and Cu dispersions were determined by $\text{H}_2\text{-O}_2\text{-H}_2$ titration and N_2O chemisorption, respectively, using a PCA-1200 apparatus. Transmission electron microscope (TEM) images were obtained on a Thermo Fisher Scientific Titan Themis-Z microscope. X-ray photoelectron spectra (XPS) were carried out using an Axis Ultra DLD (Kratos Tech.) set up with an Al $\text{K}\alpha$ source. Raman spectra of catalysts were obtained by a Horiba Labram Aramis Raman spectrometer. Scanning TEM (STEM) and elemental mapping images were taken using a high-angle annular dark-field (HAADF) detector. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out using a Thermo Scientific NICOLET 6700 FTIR spectrometer equipped with Harrick praying mantis and ZnSe window. 50 mg of KBr was added to 50 mg of the catalyst and ground into fine powder. The mixture was transferred to the in situ reaction cell and treated using the same reaction conditions but atmosphere pressure. The infrared spectra were continuously collected for about 90 min.

3. RESULTS and DISCUSSION

3.1 Characterization of a series supports

Fig. 1. Wide angle XRD spectra of the various supports.

XRD patterns of different supports are shown in Fig. 1. Pure CeO_2 and all the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composites show four prominent characteristic peaks, which can be assigned to (111), (200), (220), and (311) crystal faces of CeO_2 with face-centered cubic (FCC) fluorite structure [38]. The characteristic peaks of the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composites are shifted towards the high angle direction because of the Zr element embedded into the framework of CeO_2 [39]. Pure ZrO_2 support exhibits the characteristic peaks of monoclinic ZrO_2 [40]. None of the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composites (CZ-1, CZ-2 and CZ-3), and pure CeO_2 , show any characteristic peaks of the ZrO_2 phase, indicating that the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution composites were successfully prepared [41].

SEM images of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composites, pure CeO_2 and ZrO_2 are shown in Fig. 2. CZ-1 and CZ-2 composites exhibit defective wrinkled spherical particles. Compared with CZ-1 and CZ-2 composites, CZ-3 displays relatively uniform wrinkled spherical particles, which are beneficial to improve the specific surface area, thus promoting the dispersion of the active metals on the support surface. The particle sizes of all ZrO_2 are slightly bigger than the hard template DMSNs. Pure CeO_2 support shows relatively scattered and irregular fine particles, while pure ZrO_2 presents large lump-like particles.

Fig. 2. SEM images of the various materials.

Fig. 3. TEM images of various materials.

TEM images of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composites, pure CeO_2 and ZrO_2 are displayed in Fig. 3. Pure CeO_2 , CZ-1 and CZ-2 composites exhibit a defective dendritic spherical structure, presumably due to the high content of CeO_2 , thus resulting in poor thermal stability and the exfoliation of a portion of the dendritic spherical particles. CZ-3

support displays a much more uniform dendritic structure than those of CZ-1 and CZ-2 composites, which can improve the accessibility between the reactive metal and the reactant molecules and reduce the diffusion resistance of the reactant and products on the catalyst surface. In contrast, pure ZrO_2 presents relatively large particles, making it difficult to remove the hard template DMSNs altogether. Moreover, CZ-3 support exhibits a small particle size of about 200 nm.

3.2 Characterization of catalysts

Fig. 4. (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of catalysts.

Fig. 4a and b exhibit N_2 adsorption-desorption isotherms and pore size distributions of a series of dendritic PdCu/CZ catalysts, PdCu/CeO₂, and PdCu/ZrO₂. All the N_2 adsorption-desorption isotherms exhibit type-IV curves with H2 hysteresis loops, suggesting dendritic PdCu/CZ catalysts, PdCu/CeO₂ and PdCu/ZrO₂ catalysts all possess mesoporous structures. The PdCu/CZ-3 catalyst's hysteresis loop is relatively wide, indicating that the PdCu/CZ-3 catalyst contains different pore sizes with a slit shape pore. Fig. 4b displays that the pore size distributions of these dendritic PdCu/CZ catalysts are narrower than that of PdCu/CeO₂ catalyst.

The texture parameters of this series of dendritic PdCu/CZ catalysts, PdCu/CeO₂, and PdCu/ZrO₂ catalysts are listed in Table 1. PdCu/CZ-3 with a uniform dendritic structure possesses the highest surface area ($125 \text{ m}^2 \text{ g}^{-1}$), relatively high pore volume ($0.41 \text{ cm}^3 \text{ g}^{-1}$), and suitable pore diameter (13.8 nm), which can promote the

dispersion of the active metals on the support surface. Compared with the texture parameter of these dendritic CZ composites, pure CeO_2 and ZrO_2 support (Fig. S1 and Table S2, Supporting Information), the surface areas and pore volumes decrease slightly after the addition of PdCu active metals. The Pd metal dispersion degree (23.6 %) and Cu metal dispersion degree (13.9 %) of dendritic PdCu/CZ-3 catalyst are higher than those of other PdCu/CZ catalysts, PdCu/ CeO_2 , and PdCu/ ZrO_2 catalysts due to the higher surface area and pore volume of CZ-3 support.

Table 1. Textural parameter of various catalysts.

Catalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{mes} ($\text{cm}^3 \text{g}^{-1}$)	d_{BJH} (nm)	Metal disp. ^a (%)	
				Pd	Cu
PdCu/ CeO_2	76	0.45	23.6	13.5	7.2
PdCu/CZ-1	75	0.29	16.1	16.8	9.3
PdCu/CZ-2	105	0.39	14.5	19.1	11.6
PdCu/CZ-3	125	0.41	13.8	23.6	13.9
PdCu/ ZrO_2	26	0.10	13.8	9.3	5.8

^a Metal dispersion determined by H_2 - O_2 - H_2 titration for Pd and N_2O titration for Cu.

Many distinct lattice fringes with a lattice spacing of 0.31 nm can be found in Fig. 5a and b, attributed to the (111) crystal plane of dendritic CZ-3 composite [38]. The EDS mappings (Fig. 5c-h) indicate that PdCu alloy, Pd, Cu, Ce, Zr, and O are uniformly dispersed. PdCu active metals are better distributed over dendritic CZ-3 composite than pure ZrO_2 support (Fig. S2, Supporting Information).

Fig. 5. HAADF-STEM and EDS (PdCu alloy, Pd, Cu, Ce, Zr, O) pictures of PdCu/CZ-3.

Fig. 6. XPS spectra of Ce 3d (A), O 1s (B), Pd 3d (C) and Cu 2p (D) over (a) PdCu/CeO₂, (b) PdCu/CZ-3, (c) PdCu/ZrO₂, (d) spent PdCu/CZ-3 and (e) spent PdCu/ZrO₂.

Table 2. XPS deconvolution results of Ce (3d), O (1s), Pd (3d) and Cu (2p) over series catalysts.

Catalysts	Ce species (%)			O species (%)			Pd species (%)			Cu species (%)	
	Ce ³⁺	Ce ⁴⁺	R ^a	O ²⁻	O ₂ ²⁻	O ₂ ⁻	Pd ⁰	Pd ²⁺	R ^b	Cu ⁰	Cu ²⁺
PdCu/CeO ₂	24.5	75.5	32.5	40.5	5.3	54.2	23.7	76.3	31.1	0	100
PdCu/CZ-3	35.8	64.2	55.8	34.6	9.4	56.0	31.5	68.5	46.0	0	100
PdCu/ZrO ₂	-	-	-	47.7	7.8	44.5	9.4	90.6	10.4	0	100
Spent PdCu/CZ-3	37.2	62.8	59.2	38.0	12.1	49.9	100	0		100	0
Spent PdCu/ZrO ₂	-	-	-	45.2	6.5	48.3	100	0		100	0

^a The Ce species ratio of Ce³⁺/Ce⁴⁺.

^b The Pd species ratio of Pd⁰/Pd²⁺.

XPS characterizations of PdCu/CeO₂, PdCu/CZ-3, PdCu/ZrO₂, spent PdCu/CZ-3 and spent PdCu/ZrO₂ catalysts were used to investigate the chemical state of Ce, O, Pd and Cu elements, and the corresponding deconvolution results of Ce (3d), O (1s), Pd (3d), and Cu (2p) are displayed in Fig. 6 and Table 2. Fig. 6A presents Ce 3d deconvolution results of PdCu/CeO₂, PdCu/CZ-3 and spent PdCu/CZ-3 catalysts. The position of characteristic peaks of the PdCu/CZ-3 and spent PdCu/CZ-3 catalysts is shifted towards the higher binding energy due to the addition of ZrO₂. The PdCu/CZ-3 and spent PdCu/CZ-3 catalysts all show a higher Ce³⁺/Ce⁴⁺ ratio than PdCu/CeO₂ catalyst (R^a, Table 2), manifesting that the addition of ZrO₂ can induce more Ce⁴⁺ cations to transform into activated Ce³⁺. A higher Ce³⁺/Ce⁴⁺ ratio in the PdCu/CZ-3 catalyst is conducive to the generation of more oxygen vacancies, thus promoting the adsorption and activation of CO₂ in the CO₂ hydrogenation reaction process [34]. O 1s deconvolution results of PdCu/CeO₂, PdCu/CZ-3, PdCu/ZrO₂, spent PdCu/CZ-3, and spent PdCu/ZrO₂ catalysts are shown in Fig. 6B [34, 41]. The position of characteristic peaks of the PdCu/CZ-3, PdCu/ZrO₂, spent PdCu/CZ-3 and spent PdCu/ZrO₂ catalysts are shifted towards to the higher binding energy due to the addition of ZrO₂ and the reduction by H₂. The PdCu/CZ-3 and spent PdCu/CZ-3 catalysts all exhibit higher active oxygen ratios (O₂²⁻ and O₂⁻) than PdCu/CeO₂ catalyst, PdCu/ZrO₂, and spent PdCu/ZrO₂ (Table 2), which can promote the adsorption and activation of CO₂ in the CO₂ hydrogenation. Pd 3d, Cu 2p and Cu LMM of deconvolution results of PdCu/CeO₂, PdCu/CZ-3, PdCu/ZrO₂, spent PdCu/CZ-3 and spent PdCu/ZrO₂ catalysts are shown in Fig. 6C, 6D and Fig. S3, respectively. The intensities of the peaks assigned to Pd and Cu of PdCu/CZ-3 and spent PdCu/CZ-3 catalysts are weaker than PdCu/CeO₂, PdCu/ZrO₂ and spent PdCu/ZrO₂ catalysts, which means PdCu metals are better dispersed on the surface of dendritic CZ-3 composite. The ratios of metallic Pd⁰ and Cu⁰ of spent PdCu/CZ-3 and spent PdCu/ZrO₂ catalysts are all 100% (Table 2), manifesting that all the PdCu species of series catalysts are reduced to metallic state at the CO₂ hydrogenation reaction conditions (Fig. S3, in Supporting Information).

Fig. 7. Wide angle XRD (A), H₂-TPD (B), CO₂-TPD (C) and H₂-TPR (D) profiles of (a) PdCu/CeO₂, (b) PdCu/CZ-1, (c) PdCu/CZ-2, (d) PdCu/CZ-3 and (e) PdCu/ZrO₂.

Wide-angle XRD, H₂-TPD, CO₂-TPD and H₂-TPR profiles of PdCu/CeO₂, PdCu/CZ-1, PdCu/CZ-2, PdCu/CZ-3 and PdCu/ZrO₂ are exhibited in Fig. 7. The XRD characteristic peaks (Fig. 7A) of these catalysts are essentially the same as the XRD characteristic peaks of corresponding supports (Fig. 1), indicating that the supports retain their original structures after loading the active PdCu metals. Moreover, Pd and Cu's characteristic peaks were not detected in the XRD profiles of these catalysts, indicating that the PdCu metals are well distributed on the support surface. H₂-TPD profiles (Fig. 7B) of dendritic PdCu/CZ catalysts, PdCu/CeO₂, and PdCu/ZrO₂ catalysts show that all catalysts display two prominent characteristic peaks at 50–150 °C and 200–400 °C, respectively. The characteristic peak at 50–150 °C is attributed to the hydrogen adsorbed on PdCu metals, while another characteristic peak

at 200–400 °C is assigned the hydrogen heterolytically adsorbed on the supports [42, 43]. The pure support can easily chemisorb hydrogen with the addition of PdCu metals, which can be explained by hydrogen spillover from PdCu metals onto the support, resulting in the synergistic effect between the PdCu metals and the supports [44, 45]. The desorption temperature of PdCu/CZ-3 catalyst is shifted towards the lower temperature at 50–150 °C, indicating that the highly dispersed PdCu metals are more conducive to hydrogen spillover from Pd to Cu surface [46]. The H₂ amount desorbed from PdCu/CZ-3 catalyst (Table S4, Supporting Information) is higher than other dendritic PdCu/CZ catalysts, PdCu/CeO₂ and PdCu/ZrO₂ catalysts because of the improvement of the hydrogen spillover from PdCu metals onto the dendritic CZ-3 surface. Moreover, the spillover hydrogen from the PdCu metals can induce more Ce⁴⁺ cations to transform into activated Ce³⁺. CO₂-TPD profiles (Fig. 7C) of dendritic PdCu/CZ catalysts, PdCu/CeO₂ and PdCu/ZrO₂ catalysts were carried out to investigate the oxygen vacancies on the support surface. All catalysts display two characteristic peaks at 50–150 °C and 300–600 °C, respectively. The characteristic peak at 50–150 °C is attributed to the CO₂ physically adsorbed on the supports. The wide characteristic peak at 300–600 °C is assigned to the CO₂ adsorbed in the oxygen vacancies generated by thermal treatment [47]. The CO₂ amount desorbed from dendritic PdCu/CZ-3 catalyst (Table S4, Supporting Information) is higher than other dendritic PdCu/CZ catalysts, PdCu/CeO₂, and PdCu/ZrO₂ catalysts, manifesting the generation of more oxygen vacancies in the uniform dendritic PdCu/CZ-3 catalyst. H₂-TPR profiles (Fig. 7D) of dendritic PdCu/CZ catalysts, PdCu/CeO₂ and PdCu/ZrO₂ catalysts display two characteristic peaks at 100–300 °C and 300–700 °C, respectively. The characteristic peak at 100–300 °C is attributed to the reduction of PdO and CuO oxides, while another characteristic peak at 300–600 °C is assigned the reduction of the support oxides [48]. The low-temperature peak of dendritic PdCu/CZ-3 is wider than those of other catalysts, indicating that more active species can be reduced due to the higher dispersion degree on the PdCu/CZ-3 catalyst. The high-temperature peak of dendritic PdCu/CZ-3 is shifted towards the lower temperature, manifesting that the enhanced hydrogen spillover helps to reduce the

dendritic CZ-3 composite [49].

Fig. 8. Raman patterns of a series of catalysts.

Raman spectra of PdCu/CeO₂, PdCu/CZ-3, and spent PdCu/CZ-3 catalysts are exhibited in Fig. 8. The characteristic peak of PdCu/CeO₂ at 435 cm⁻¹ is assigned to the represent peak of CeO₂. Raman characteristic peak at 627 cm⁻¹ is attributed to the double degeneration into a longitudinal optical mode of CZ, related to the formation of oxygen vacancies on the support surface [34]. No Raman characteristic peak at 627 cm⁻¹ is detected over the PdCu/CeO₂ catalyst, while PdCu/CZ-3 and spent PdCu/CZ-3 catalysts show a distinct characteristic peak at 627 cm⁻¹, indicating the addition of the ZrO₂ to the CZ-3 composite can promote the generation of more oxygen vacancies, consistent with the observations by XPS.

3.3 Catalytic activity and CO₂ hydrogenation mechanism

Fig. 9. (a) CO₂ conversion and (d) MeOH yield as a function of temperature; (b) CO₂ conversion and (e) MeOH yield as a function of reaction pressure; (c) CO₂ conversion and (f) MeOH yield as a function of GHSV; (g) CO₂ conversion and (h) MeOH yield on 100 h time of stream at standard reaction conditions over a series of catalysts. Standard reaction conditions: CO₂/H₂ = 1/3, 250 °C, 5.0 MPa and GHSV = 3600 mL gcat⁻¹ h⁻¹ (STP)

The effect of reaction temperature, pressure, and GHSV on the CO₂ conversion and MeOH yield of CO₂ hydrogenation over PdCu/CeO₂, PdCu/CZ-1, PdCu/CZ-2, PdCu/CZ-3, and PdCu/ZrO₂ are exhibited in Fig. 9a-f. PdCu/CZ-3 catalyst shows the highest CO₂ conversion and MeOH yield compared to PdCu/CeO₂, PdCu/CZ-1, PdCu/CZ-2, and PdCu/ZrO₂ catalysts under all conditions. Besides, the MeOH

selectivity of series catalysts at different reaction conditions is provided in Fig. S4 (Supporting Information). The other main byproduct was CO with CH₄ selectivity always being lower than 0.2%. The CO₂ conversions of these catalysts all increase with the increasing reaction temperatures (Fig. 9a). The MeOH yield of all the catalyst showed an increasing trend with increasing temperature and reached its maximum at 300 °C (Fig. 9d). The CO₂ conversions and MeOH yields of these catalysts increase with rising reaction pressures (Fig. 9b and e). The CO₂ conversions and MeOH yields of these catalysts increase with the decreasing GHSVs (Fig. 9c and f). 100 hours on stream experiments of these catalysts were also studied (Fig. 9g and h). The CO₂ conversion and MeOH yield of PdCu/CZ-3 catalyst are maintained over this long period on stream, while the CO₂ conversions and MeOH yields of PdCu/CeO₂, PdCu/CZ-1, PdCu/CZ-2, and PdCu/ZrO₂ catalysts all show a downward trend in various degrees. PdCu/CZ-3 displays the highest CO₂ conversion, highest MeOH yield, and the best stability among PdCu/CeO₂, PdCu/CZ-1, PdCu/CZ-2, and PdCu/ZrO₂.

Fig. 10. (A) MeOH formation rate and (B) Arrhenius plots over PdCu/Ce_xZr_{1-x}O₂ catalysts.

Reaction conditions: $\text{CO}_2/\text{H}_2 = 1/3$, 5.0 MPa and $\text{WHSV} = 3600 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ (STP). (C) Changes of monometallic- and bimetallic-based CH_3OH TOFs of $\text{PdCu}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts. Reaction conditions: $\text{CO}_2/\text{H}_2 = 1/3$, 250 °C, 5.0 MPa and $\text{WHSV} = 3600 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ (STP). (a) PdCu/CeO_2 , (b) $\text{PdCu}/\text{CZ-1}$, (c) $\text{PdCu}/\text{CZ-2}$, (d) $\text{PdCu}/\text{CZ-3}$ and (e) PdCu/ZrO_2 .

Fig. 10A displays the MeOH formation rate of series $\text{PdCu}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts at different temperatures. The $\text{PdCu}/\text{CZ-3}$ exhibits the highest MeOH formation rate, with an STY ($2.18 \text{ mol}_{\text{MeOH}} \text{ kg}^{-1} \text{ h}^{-1}$) more than six times that of PdCu/CeO_2 ($0.36 \text{ mol}_{\text{MeOH}} \text{ kg}^{-1} \text{ h}^{-1}$), and more than 54 times that of PdCu/ZrO_2 ($0.04 \text{ mol}_{\text{MeOH}} \text{ kg}^{-1} \text{ h}^{-1}$) at 250 °C. The Arrhenius plots (Fig. 10B) based on PdCu of series $\text{PdCu}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts were studied to calculate the apparent activation energies (E_a) [50]. The E_a values for $\text{PdCu}/\text{CZ-3}$ ($20.8 \pm 0.6 \text{ kJ mol}^{-1}$) is distinctly lower than for PdCu/CeO_2 ($36.9 \pm 1.1 \text{ kJ mol}^{-1}$) and PdCu/ZrO_2 ($46.8 \pm 0.9 \text{ kJ mol}^{-1}$) catalysts, suggesting that $\text{PdCu}/\text{CZ-3}$ is more intrinsically active for CO_2 hydrogenation. The turnover frequencies (TOFs) of series $\text{PdCu}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts were estimated based on the surface Pd and Cu atoms determined by CO and N_2O chemisorption, respectively. The normalized TOFs of series $\text{PdCu}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts based on single Pd , single Cu , and PdCu are exhibited in Fig. 10C. The TOF value of MeOH formation based on PdCu of $\text{PdCu}/\text{CZ-3}$ (7.7 h^{-1}) is more than 2.8 times higher than over the PdCu/CeO_2 (2.7 h^{-1}), and more than 3.5 times higher than over PdCu/ZrO_2 (2.2 h^{-1}).

Fig. 11. In situ DRIFTS spectra of (a) PdCu/CeO_2 and (b) $\text{PdCu}/\text{CZ-3}$.

Reaction conditions: $\text{CO}_2/\text{H}_2 = 1/3$, 250 °C, 0.1 MPa and $\text{WHSV} = 3600 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ (STP).

In situ DRIFTS measurements (Fig. 11) were performed to study the intermediates and MeOH correlation. Three prominent characteristic peaks of

PdCu/CZ-3 and PdCu/CeO₂ at 2840, 2908, and 2950 cm⁻¹ can be found, attributed to CH₂O*, CH₃O* and HCOO*, respectively [51-53]. These three species are intermediates during the CO₂ hydrogenation reaction over PdCu/CZ-3 and PdCu/CeO₂. Based on the recent literature [54-56], the CO₂ hydrogenation reaction over PdCu/CZ-3 and PdCu/CeO₂ is likely to proceed via the CO₂ → HCOO* → HCOOH → CH₂O* → CH₃O* → CH₃OH steps.

Fig. 12. Models of different catalyst surface: (a) PdCu/CeO₂, (b) PdCu/CeO₂ with one oxygen vacancy, (c) PdCu/CZ, (d) PdCu/CZ with one oxygen vacancy. The formation energy of oxygen vacancy was calculated as: $E_{ov} = E_v + 1/2E_{O_2} - E_p$. E_v represents energy of the defect system, E_p represents energy of the perfect system, and E_{O_2} represents energy of a free oxygen molecule in the gas phase.

DFT modeling of the PdCu/CeO₂ and PdCu/CZ catalyst surfaces was performed (Fig. 12) to obtain the formation energies of oxygen vacancies. Based on the DFT calculation results, it can be found that the formation energy of O vacancy is 4.07 eV on the PdCu/CZ catalyst compared to 4.52 eV on the PdCu/CeO₂ catalyst, meaning that the introduction of Zr species into the CeO₂ support is beneficial for the creation of O vacancy. The DFT calculation results are in agreement with XPS and CO₂-TPD characterizations.

Fig. 13. (a) The calculated energy profile for HCOO* formation in the presence of oxygen vacancy on the PdCu/CeO₂ and PdCu/CZ catalysts, the formation pathways and corresponding configurations of HCOO* in the presence of oxygen vacancy on the (b, d) PdCu/CeO₂ and (c, e) PdCu/CZ catalyst.

In order to investigate the formation of HCOO* intermediate, the adsorptions of CO₂ on the surface O vacancy of both catalyst surfaces were calculated by DFT methods (Fig. 13). The adsorption energies for CO₂ were -0.74 eV and -1.08 eV on the PdCu/CeO₂ and PdCu/CZ catalysts, respectively. In addition, the reaction barrier of the formation of HCOO* was 1.58 eV on the PdCu/CZ catalyst, smaller than that of the PdCu/CeO₂ catalyst (2.22 eV), strongly indicating that dendritic PdCu/CZ catalyst indeed increases the concentration of HCOO* intermediate, which is considered to be beneficial for the CH₃OH formation.

Combined DFT calculation results and in situ DRIFTS results, we can find that the CZ support plays the role of adsorbing the CO₂ molecules due to its higher amount of oxygen vacancies. The oxygen vacancy of CZ support can lower the adsorption energy of CO₂. Moreover, the reaction barrier of the formation of HCOO* on the PdCu/CZ catalyst is smaller than that of the PdCu/CeO₂ catalyst. Besides, PdCu alloy can promote the dissociation of hydrogen, which can provide active hydrogen for the CO₂ hydrogenation reaction on the CZ support. Therefore, the higher

CO₂ hydrogenation to methanol performance of PdCu/CZ-3 catalyst is due to the synergistic effect of dendritic CZ-3 support and PdCu alloy.

3.4 Discussion

PdCu/Ce_xZr_{1-x}O₂ catalysts with uniform dendritic spherical structures and superior surface properties were successfully prepared and were used to produce MeOH from CO₂ hydrogenation reaction. The higher surface area and higher number of oxygen vacancies for PdCu/CZ-3, along with a uniform dendritic particle size, resulted in excellent CO₂ conversion (25.5%) and methanol yield (6.4%) with a superior PdCu-TOF_{MeOH} of 7.7 h⁻¹ (Fig. 9 and 10). The correlation between the activity and surface properties was observed. The wrinkled surface (Fig. 2) of CZ-3 composite can improve its specific surface area and pore volume (Fig. 2 and Table 1), thus promoting the dispersion (Fig. 5 and 6) of the PdCu active metals on the support surface. The PdCu active metal with a higher dispersion degree is conducive to the dissociation of hydrogen on its surface, and the generated activated hydrogen will spillover onto the surface (Fig. 7B and 7D) of the CZ-3 support. The spillover hydrogen enhances the oxygen vacancies of the CZ-3 support and promotes the CO₂ hydrogenation reaction on the surface of PdCu/CZ-3. The open dendritic pore structure and small particle sizes (Fig. 3) of PdCu/CZ-3 improve the accessibility between the PdCu metals and CO₂ and H₂ molecules, and at the same time reduces the diffusion resistance of the reactants and products on the catalyst surface, thus improving the CO₂ conversion and MeOH yield of CO₂ hydrogenation reaction over PdCu/CZ-3 (Fig. 9). The addition of ZrO₂ can induce more Ce⁴⁺ cations to transform into activated Ce³⁺ over PdCu/CZ-3 (Fig. 6 and Table 2). More Ce³⁺ cations on PdCu/CZ-3 enable the generation of more oxygen vacancies (Fig. 6B and 8), leading to the enhancement in the adsorption and activation of CO₂ in the CO₂ hydrogenation reaction (Fig. 7C). DFT calculations on the formation energy of oxygen vacancy also display that the introduction of Zr species into the CeO₂ support is beneficial for creating O vacancy (Fig. 12). PdCu/CZ-3 can also promote the generation of the formate species (HCOO*) and methoxy species (CH₂O* and CH₃O*) because of the

synergistic effect of hydrogen spillover and oxygen vacancies on the surface of PdCu/CZ-3. DFT calculations on the energy profile of HCOO* formation also show that the dendritic PdCu/CZ catalyst indeed increases the concentration of HCOO* intermediate (Fig. 13). The formate species and methoxy species are the key intermediates to produce MeOH (Fig. 11). Furthermore, PdCu/CZ-3 exhibits relatively high thermal stability after the addition of ZrO₂, resulting in a long time on stream stability for over 100 hours (Fig. 9g and 9h).

4 CONCLUSION

Novel dendritic PdCu/Ce_{0.3}Zr_{0.7}O₂ catalyst with highly dispersed active metals and more oxygen vacancies was used for CO₂ hydrogenation reaction. The open dendritic pore channel of PdCu/CZ-3 catalyst was found to decrease the reactants and products' diffusion resistance and boost the accessibility of PdCu active sites to H₂ and oxygen vacancy to CO₂. PdCu/CZ-3 catalyst displayed higher spillover hydrogen and more oxygen vacancies, which improved the adsorption and activation ability of CO₂ during the CO₂ hydrogenation process. The improvement of formate and methoxy pathways plays a vital role in accelerating CO₂ hydrogenation. Dendritic PdCu/CZ-3 catalyst exhibited the highest CO₂ conversion, highest MeOH yield and highest PdCu-TOF_{MeOH}, and the highest 100 h long-term stability than those of other dendritic PdCu/Ce_xZr_{1-x}O₂ and reference PdCu/CeO₂ and PdCu/ZrO₂ catalysts. Dendritic PdCu/CZ-3 catalyst has great potential value in the field of CO₂ hydrogenation.

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Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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