# **Supplementary Information**

# Engineering nanoscale H supply chain to accelerate methanol synthesis on ZnZrO<sub>x</sub>

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#### 1. Methods

## Materials

 $Zn(NO_3)_2 \cdot 6H_2O$  (98%),  $ZrO(NO_3)_2 \cdot xH_2O$  (99%),  $(NH_4)_2CO_3$  ( $\geq 30\%$  NH<sub>3</sub> basis) and Pd(NO<sub>3</sub>)\_2 \cdot xH\_2O (40% Pd basis) were purchased from Sigma Aldrich. CNT (multiwalled carbon nanotube, ANR technologies), AC (activated carbon, Sigma Aldrich), and GNP (graphene nanoplatelets, Sigma Aldrich) were used after washing with a 6 M HCl aqueous solution (30 cm<sup>3</sup> g<sup>-1</sup>) to remove metal impurities, whereas SiO<sub>2</sub> (Davisil grade 633) and TiO<sub>2</sub> (Degussa P25) were used without any treatment.

#### **Catalysts preparation**

**Synthesis of ZnZrO**<sub>x</sub>. ZnZrO<sub>x</sub> solid solution catalyst was prepared by a coprecipitation method. Typically, 10.6 g of Zn(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$  and 11.3 g of ZrO(NO<sub>3</sub>)<sub>2</sub>· $xH_2O$  were dissolved in 140 cm<sup>3</sup> of deionized (DI) water at 343 K. The precipitant, 0.625 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> aqueous solution 100 cm<sup>3</sup>, was added dropwise to the aforementioned solution under vigorous stirring. The suspension was aged for 2 h at 343 K under vigorous stirring (800 rpm). After cooling down to room temperature, the precipitate was recovered by filtration and washed thoroughly with DI water. The resulting gel was dried at 373 K for 12 h and calcined at 773 K under air flow for 3 h.

**Synthesis of Pd/ZnZrO**<sub>x</sub>. 1 wt% Pd was supported on as-prepared ZnZrO<sub>x</sub> by incipient wetness impregnation using aqueous Pd(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O solution. After the evaporation of the solvent at 343 K, the sample was dried at 373 K for 12 h. The dried sample was calcined and reduced at 673 K under dry air and 5%H<sub>2</sub>/N<sub>2</sub> flow for 2 h, respectively.

**Synthesis of Pd/CNT+ZnZrO<sub>x</sub>.** 2 wt% Pd supported on CNT (Pd/CNT) was prepared by incipient wetness impregnation using aqueous Pd(NO<sub>3</sub>)<sub>2</sub>·*x*H<sub>2</sub>O solution. After the evaporation of the solvent at 343 K, the sample was dried at 373 K for 8 h, followed by reducing at 673 K for 2 h under 5%H<sub>2</sub>/N<sub>2</sub> flow. The reduced Pd/CNT was physically mixed with as-prepared ZnZrO<sub>x</sub> by mortar grinding with Pd:ZnZrO<sub>x</sub> = 1:100 mass ratio (i.e. Pd/CNT:ZnZrO<sub>x</sub> = 1:2 mass ratio).

**Synthesis of other physically mixed catalysts.** Various 2 wt% Pd supported catalysts, Pd/AC, Pd/GNP, Pd/SiO<sub>2</sub>, Pd/TiO<sub>2</sub>, were prepared by incipient wetness impregnation using aqueous Pd(NO<sub>3</sub>)<sub>2</sub>·*x*H<sub>2</sub>O solution. The evaporation and drying methods are similar to those employed in the synthesis of Pd/CNT. For Pd/AC and Pd/GNP, the dried sample was reduced at 673 K for 2 h under 5%H<sub>2</sub>/N<sub>2</sub> flow. For Pd/SiO<sub>2</sub> and Pd/TiO<sub>2</sub>, the dried sample was calcined and reduced at 673 K for 2 h under dry air and 5%H<sub>2</sub>/N<sub>2</sub> flow, respectively. The reduced Pd/*support* catalysts were physically mixed with as-prepared ZnZrO<sub>x</sub> at Pd:ZnZrO<sub>x</sub> = 1:100 mass ratio by mortar grinding. CNT+Pd/ZnZrO<sub>x</sub> was prepared by mortar grinding of CNT and as-prepared Pd/ZnZrO<sub>x</sub> (CNT:Pd/ZnZrO<sub>x</sub> = 1:2 mass ratio). CNT+ZnZrO<sub>x</sub> was prepared by mortar grinding of CNT and as-prepared ZnZrO<sub>x</sub> (CNT:ZnZrO<sub>x</sub> = 1:2 mass ratio).

**Preparation of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts.** A commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst was purchased from Alfa Aesar (Product no. 45776). Lab-made Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by

coprecipitation of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (>98%, Sigma Aldrich), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (>98%, Sigma Aldrich) with Na<sub>2</sub>CO<sub>3</sub> (anhydrous, Sigma Aldrich) as precipitant. 4.35 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 2.68 g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and 1.12 g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Cu/Zn/Al = 6/3/1 molar) were dissolved in 100 cm<sup>3</sup> of DI water at 343 K. The precipitant, 0.3 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution 120 cm<sup>3</sup>, was added dropwise to the aforementioned solution under vigorous stirring. The suspension was aged for 2 h at 343 K under vigorous stirring (800 rpm). After cooling to room temperature, the precipitate was recovered by filtration and washed thoroughly with DI water. The resulting gel was dried at 353 K for 12 h and calcined at 623 K under air flow for 3 h.

## **Catalyst characterization**

Transmission electron microscopy (**TEM**) was performed using a JEM 2100F (JEOL) operating at 200 kV. Prior to the analysis, the powdery samples were dispersed in ethanol (HPLC grade) and placed on a Formvar-coated copper grid. The number-weighted average particle size of Pd was determined by the equation

$$d_{\text{Pd}} = \frac{\sum d_i n_i}{\sum n_i}$$
, where  $d_i$  is the particle diameter, and  $n_i$  is the number of particles with this diameter. (1)

Energy dispersive X-ray (EDX) elemental mapping was conducted in an Oxford instrument during TEM analysis.

Scanning electron microscopy (SEM) was performed using a JSM-7610Plus (JEOL) microscope operating at 5 kV and 32.8  $\mu$ A.

Powder X-ray diffraction (**XRD**) patterns were collected using a D2-Phaser diffractometer equipped with a Cu K $\alpha$  radiation source (40 kV, 30 mA) and a LYNXEYE detector (Bruker). The data were monitored at a resolution of 0.02 degree and count time of 0.2 s for each point.

N<sub>2</sub> physisorption at 77 K was performed using a NOVAtouch NT 4LX-1 volumetric analyzer (Quantachrome). Prior to the measurement, samples were degassed at 623 K for 3 h under high vacuum. Brunauer–Emmett–Teller surface area ( $S_{BET}$ ) were determined in the  $P/P_0$  range of 0.10–0.30 of the N<sub>2</sub> adsorption branch.

H<sub>2</sub> and CO chemisorption were performed using a Micromeritics ASAP2020 volumetric analyzer. Prior to the measurement, samples were re-reduced at 673 K for 2 h under H<sub>2</sub> flow, and evacuated under high-vacuum at the same temperature for 2 h. To avoid formation of Pd hydrides, the measurements were performed at 343 K. The amount of chemisorption was estimated by extrapolation of the linear portion of the isotherm (5–30 kPa) and the dispersion of Pd particles was determined by using the stoichiometry factors: Pd/H = 1,<sup>1</sup> and Pd/CO = 0.5.<sup>2</sup>

CO<sub>2</sub> temperature-programmed desorption (**CO<sub>2</sub>-TPD**) profiles were recorded using a BELCAT II catalyst analyser equipped with a thermal conductivity detector. Typically, 0.1 g of sample was pretreated under H<sub>2</sub> flow (30 cm<sup>3</sup> min<sup>-1</sup>) at 673 K. Then, CO<sub>2</sub> (30 cm<sup>3</sup> min<sup>-1</sup>) was dosed to sample at 323 K for 1 h and the weakly adsorbed CO<sub>2</sub> was removed by He flow (30 cm<sup>3</sup> min<sup>-1</sup>) for 1 h at the same temperature. For the measurement of the TPD profiles, the temperature was increased up to 673 K (ramp: 10 K min<sup>-1</sup>) under He flow (30 cm<sup>3</sup> min<sup>-1</sup>). The adsorbed amount of CO<sub>2</sub> was determined in the temperature range of 323–673 K of the profile.  $H_2$  temperature-programmed desorption (H<sub>2</sub>-TPD) profiles were measured similarly with CO<sub>2</sub>-TPD changing the adsorbate to  $H_2$ . The adsorbed amount of  $H_2$  was determined in the temperature range of 323–533 K of the profile.

 $H_2-D_2$  isotope exchange was carried out using a plug flow quartz reactor at ambient pressure with an online quadrupole mass spectrometer (ThermoStar-GSD 320) following the earlier literature.<sup>3</sup> Typically, 20 mg of catalyst was pre-reduced under H<sub>2</sub> flow at 673 K for 2 h and purged with Ar flow for 2 h at the same temperature. After cooling down to 373 K, a mixture of H<sub>2</sub> (10 kPa) and D<sub>2</sub> (10 kPa) was injected into the reactor.

**UV-Vis-NIR spectra** of the materials were taken using a Shimadzu optical spectrometer in reflectance mode. The bandgap of material was determined by Tauc plot and baseline method proposed by Makuła et al.<sup>4</sup>

$$(\frac{(1-R)^2}{2R}hv)^n = A(hv - E_g),$$
(2)

where *R* is reflectance, *hv* is the photon energy, *A* is a proportionality constant, and  $E_g$  is the bandgap. The exponent *n* denotes the nature of transition. The values for *n* (0.5 for metal oxides, and 3 for carbons) were adopted according to the literature.<sup>4,5</sup>

**X-ray photoelectron spectroscopy (XPS)** were carried out using a Thermo Scientific ESCALAB250 with a Al K $\alpha$  monochromatic X-ray source (hv = 1486.6 eV, 9 mA, 15 kV). The gas treatments were carried out using a labmade *in situ* cell and gas flowing system to prevent air exposure. Typically, the spectra ware measured after the given gas treatment and subsequent cooling to room temperature, He purging, and evacuation. The spectra denoted as pristine were measured after degassing using He flow at 673 K for 2 h. Next, samples were treated by H<sub>2</sub> at 673 K for 2 h. After cooling down to room temperature, the *in situ* cell was purged by He for 1 h to desorb weakly bound adsorbates. The sample was introduced into the XPS chamber without any air exposure and spectra were recorded at room temperature under the ultrahigh vacuum condition. The sequential spectra measurement after CO<sub>2</sub> (at 533 K) and CO<sub>2</sub>+H<sub>2</sub> (1:4 ratio, at 533 K) treatment were carried out similarly. The peak deconvolution was conducted by XPSpeak41 software. Baselines were made by a Shirley type background curve. To deconvolute Zn 2 $p_{3/2}$  spectra, full width at half maximum (FWHM) and Gaussian-Lorentzian% of peaks were fixed as 2.5–3.1 eV and 25–50%, respectively. The portion of Zn species in Zn 2 $p_{3/2}$  were determined by their area. Zr 3*d* spectra were first deconvoluted into a pair of Zr 3 $d_{5/2}$  and Zr 3 $d_{3/2}$  doublet with a fixed area ratio of Zr 3 $d_{5/2}$  over Zr 3 $d_{3/2}$  of 1.50. Further deconvolutions were carried out with fixed FWHM (1.35–1.60 eV) and Gaussian-Lorentzian% (10–30%) of each peak.

X-ray absorption spectroscopy (**XAS**) was conducted at beamline 01C1 at the National Synchrotron Radiation Research Center, Taiwan. The fresh ZnZrO<sub>x</sub> and Pd/CNT+ZnZrO<sub>x</sub> catalysts were transferred to *in situ* cell and pretreated with H<sub>2</sub> at 673 K for 2 h like the pretreatment of the reaction condition. For the used ZnZrO<sub>x</sub> and Pd/CNT+ZnZrO<sub>x</sub> catalysts, the samples recovered from the reactor were immediately transferred to a glass tube and sealed using a PTFE cap equipped with a Viton o-ring to minimize air exposure. Prior to XAS measurement, the used catalysts were transferred to *in situ* cell and pretreated with N<sub>2</sub> at 673 K for 2 h to degas any impurities adsorbed onto catalyst during sample transfer. Here, N<sub>2</sub> was used instead of H<sub>2</sub> to avoid any artificial reduction of the catalyst component. After cooling down the cell to room temperature, the Zn K-edge and Zr K-edge spectra were recorded in the transmission mode. The reference spectra of Zn foil, Zr foil, ZnO, and ZrO<sub>2</sub> were collected together for the comparison. The XAS spectra were analyzed using the Athena and Artemis software included in the Demeter package. The Fourier transformation of the  $k^3$ -weighted extended X-ray absorption fine structure (EXAFS) from *k* space to *R* space was carried out over the *k* range 2.0–12.6 Å<sup>-1</sup>. A part of the Fourier-transformed EXAFS in the *R* range of 1.0–2.8 Å were inversely Fourier-transformed, followed by the analysis with a curve fitting method in the *k* range of 3.0–12.0 Å<sup>-1</sup>. The back-scattering amplitude and phase shift parameters were simulated with FEFF 6L and used to perform the curve fitting procedure. The amplitude reduction factors ( $S_0^2$ ) of Zn and Zr were determined by fitting the spectra of reference Zn foil ( $S_0^2$ : 1.10) and Zr foil ( $S_0^2$ : 0.965), respectively.

#### Catalytic test and reaction kinetics study

CO<sub>2</sub> hydrogenation under various conditions were carried out using an automatic multi-channel high-pressure flow reactor. The detailed calculation procedure is represented as below.

First, the volume-change-factor (V.C.F.) was calculated by using internal standard Ar as follows:

$$V.C.F. = \frac{A_{Ar,inlet}}{A_{Ar}},$$
(3)

where  $A_{Ar,inlet}$  and  $A_{Ar}$  are the peak area of Ar in inlet and outlet, respectively.

The molar flow rate of  $CO_2$  in inlet ( $n_{CO2,inlet}$ ) was calculated as:

 $n_{\text{CO2,inlet}} \pmod{\min^{-1}} = (\text{CO}_2\% \text{ in inlet} \times 0.01) \times \text{molar reactant flow rate,}$  (4) where molar reactant flow rate is determined by flow rate (cm<sup>3</sup> min<sup>-1</sup>, STP) and gas constant (*R*).

The molar flow rate of species *i* in outlet  $(n_i)$  was calculated as follows:

 $n_i \text{ (mmol min}^{-1)} = (\text{mol}\% \text{ of species } i \text{ in outlet} \times 0.01) \times (\text{molar reactant flow rate}) \times \text{V.C.F.},$  (5) where the mol% of species i in outlet is determined by GC area of species i with prepared calibration curve. Thermal conductivity detector (TCD) was used for CO<sub>2</sub> and CO, while flame ionization detector (FID) was used for methanol, and etc.

 $CO_2$  conversion, methanol (MeOH) selectivity, and space time yield of methanol (STY<sub>MeOH</sub>) were calculated with the following equations:

$$CO_2 \text{ conversion}\% = \frac{n_{CO2,\text{inlet}} - n_{CO2}}{n_{CO2,\text{inlet}}} \times 100 \%,$$
(6)

MeOH selectivity% = 
$$\frac{n_{MeOH}}{\sum n_{product}} \times 100$$
 %, (7)

$$STY_{MeOH} (g g_{cat.}^{-1} h^{-1}) = \frac{GHSV (cm_{STP}^{3} g_{cat.}^{-1} h^{-1})}{22.4 (cm_{STP}^{3} mmol^{-1})} \times (CO_{2}\% in inlet \times 0.01) \times (CO_{2} conversion\% \times 0.01) \times (MeOH selectivity\% \times 0.01) \times Mw_{MeOH} (g mol^{-1}) \times 0.001 (mol mmol^{-1}),$$
(8)  
where  $Mw_{MeOH}$  is the molecular weight of methanol (32 g mol^{-1}).

During the long-term test, cumulative methanol production ( $Q_{MeOH}$ ) over the catalyst was calculated by integrating the STY<sub>MeOH</sub> over the time-on-stream.

 $Q_{\text{MeOH}}$  (g g<sub>cat.</sub><sup>-1</sup>) =  $\int_0^t STY_{MeOH}(t) dt$ , where *t* is time-on-stream (h).

The reaction kinetic study was conducted in low  $CO_2$  conversion regimes (see Section 3 in Supplementary Information) to avoid any mass transfer and thermodynamic limitations. Typical GHSV condition and the resultant  $CO_2$  conversion for each catalyst are represented in Supplementary Table 2. The methanol formation rate ( $r_{MeOH}$ ) was calculated by using the equation shown below.

 $r_{\text{MeOH}} \text{ (mmol } g_{\text{ZnZrOx}^{-1}} h^{-1} \text{)} = \frac{GHSV (cm_{STP}^{3} g_{cat.}^{-1} h^{-1})}{22.4 (cm_{STP}^{3} mmol^{-1})} \times (CO_{2}\% \text{ in inlet} \times 0.01) \times (CO_{2} \text{ conversion}\% \times 0.01) \times (MeOH \text{ selectivity}\% \times 0.01) \times \text{normalizing ratio} (\frac{g_{cat.}}{g_{ZnZrOx}}). \quad (10)$ Notably,  $r_{\text{MeOH}}$  is represented with respect to the mass of ZnZrO<sub>x</sub>. Typically, the normalizing ratio is 1.5 for mixture catalysts (Pd/support:ZnZrO<sub>x</sub> = 1:2 mass ratio), 1.01 for Pd/ZnZrO<sub>x</sub>, and 1.0 for standalone ZnZrO<sub>x</sub>.

The reaction order of CO<sub>2</sub> was analyzed at 533 K and 5 MPa by controlling the partial pressure of CO<sub>2</sub> ( $P(CO_2)$ ) from 0.5 to 0.95 MPa under a fixed partial pressure of H<sub>2</sub> ( $P(H_2)$ ) at 3.8 MPa, and the reaction order of H<sub>2</sub> was analysed similarly while controlling  $P(H_2)$  from 2.6 to 4.1 MPa under a fixed  $P(CO_2)$  at 0.65 MPa. Ar was used as a balance gas. To calculate the apparent activation energy ( $E_a$ ) using the Arrhenius equation, the data were acquired at 493–553 K, 5 MPa, CO<sub>2</sub>/H2/Ar = 19/76/5.

Since carbon imbalance leads to a huge error on  $CO_2$  conversion%, the carbon balance was monitored during the reaction to check the validity of the calculation method.

Carbon balance% = 
$$\frac{\sum n_{product}}{n_{CO2,inlet} - n_{CO2}} \times 100$$
 %. (11)

Typically, the carbon balance% was 99.1–99.9% during the reaction kinetic analysis and 97.9–101.1% during the long-term test.

#### **Details of computational studies**

Oxide slabs were constructed from the stable (101) plane<sup>6,7</sup> of tetragonal ZrO<sub>2</sub> bulk using the experimental lattice parameters a = b = 3.612 Å, c = 5.212 Å<sup>6,7</sup> and contained 3 layers (4 O and 2 Zr per layer, thickness of about 0.69 nm) with the bottom layer fixed in the experimental bulk positions. To obtain the experimentally suggested Zn:Zr ratio of 1:4 (Supplementary Table 1), the 1×1 ZrO<sub>2</sub>(101) surface cell (with dimensions of surface lattice vectors of 6.34 Å by 3.61 Å) was transformed, using the transformation matrix [(1,2),(-2,1)], into a supercell containing 20 O and 10 Zr atoms per layer (length of lattice vectors: 9.60 Å by 13.18 Å), and two surface Zr and two O atoms were substituted by Zn atoms, thus, obtaining a ZnZrO<sub>x</sub>(101) supercell. We also removed two surface O atoms from these models to maintain charge balance in the oxide. Based on these criteria, we constructed different models with Zn–Zn distance of 7.296 Å or 6.275 Å, and the model with the lowest relative energy was chosen for further studies (Supplementary Fig. 21 and 22). Energies of O vacancy formation were calculated as:

$$E_{O vac} = E[O vac/cat] - E[cat] + E[H_2O] - E[H_2],$$
(12)

where E[O vac/cat] is the total DFT energy of the slab with surface O vacancy, while E[cat],  $E[H_2O]$ , and  $E[H_2]$  are the total DFT energies of the unmodified slab and gas-phase  $H_2O$  and  $H_2$  molecules.

To consider O vacancies for hydrogenated surface in which 1 H atom adsorbed on O and another on Zn, all the possible position of O atom from the surface and subsurface or an OH species vicinal to H–Zn was removed; in the latter case, the vacancy formation energy is

 $E_{OH vac} = E[OH vac/cat] - E[cat] + E[H_2O] - 0.5 E[H_2],$ (13) where E[OH vac/cat] is the total DFT energy of the surface with the OH pair removed.

For the bare  $ZnZrO_x$ , the most stable model contained 2 O vacancies and a third O vacancy led to unstable structures (Supplementary Fig. 23). After hydrogenating this model, we found that further reduction of the oxide is still unfeasible due to high formation energies of the third vacancy ranging from 1.4 eV to 3.8 eV (Supplementary Fig. 24). Based on this analysis, the  $Zn_2Zr_{n-2}O_{2n-2}$  supercell containing 2 O vacancies was employed for further calculations as the most thermodynamically stable surface composition of the catalyst under reaction conditions where n is the total number of Zr atoms.

The adsorption energies of H were calculated as

$$G_{ads.} = G[H/cat] - G[cat] - 0.5 G[H_2],$$
(14)

where, G[H/cat] is the Gibbs total energy of the adsorbed system and G[cat] = E[cat] is the total energy of the isolated catalyst model.

The O-Zn pair was identified as the most stable adsorption sites for H binding on the oxide (Supplementary Fig. 25).

Graphene and CNT were built using C=C distance of 1.42 Å. We tested three CNT with diameters close to 7 Å; namely, the armchair CNT(5,5), zigzag CNT(9,0) and CNT(8,0), with calculated optical band gaps of 0.07 eV, 0.14 eV and 0.58 eV, respectively. These CNT showed adsorption energies of H varying only within 0.08 eV and our calculations using CNT(5,5) and CNT(9,0) led to the same conclusions for H adsorption on CNT/ZnZrO<sub>x</sub> and H movement from CNT to ZnZrO<sub>x</sub>. Therefore, the discussion in the main article focuses on CNT(5,5) for the sake of brevity.

Models of Pd nanoparticles supported on graphene were obtained from Wulff-constructed Pd nanoparticles truncated from the <sup>8</sup> direction with 1.56 nm diameter of the widest Pd square along {001} and 1.20 nm height (aspect ratio of 1.3) and a diameter of the Pd square at the interface of 1.16 nm, which is similar to nanoparticles observed by electron microscopic images in previous experimental studies.<sup>9,10</sup> Namely, our studies considered Pd<sub>127</sub> nanoparticle with a (100) facet in contact with a  $10 \times 10$  graphene supercell. We screened all possible high-symmetry structures of the Pd/graphene interface by aligning the center of mass of the nanoparticle to each of the high-symmetry sites of graphene and screening various rotation angles (0°, 15°, 30°, 45°, 60°, 75°, 90°) of the Pd nanoparticle around the axis normal to graphene passing through the center of mass of Pd (Supplementary Fig. 26).

The model containing CNTs in contact with  $ZnZrO_x$  surface was constructed by constructing CNT and  $ZnZrO_x$ 

supercells with closely matching lattice parameters using in-house lattice matching algorithm. In particular,  $CNT(5,5)/ZnZrO_x(101)$  model was constructed by locating (4×1) CNT(5,5) supercell compressed by 2.33% to fit with the (1×2)  $ZnZrO_x(101)$  supercell (9.61 Å by 26.37 Å combined cell) based on the aforementioned lattice parameters derived from experimental values. The compression has negligible impact in the properties of the freestanding CNT, for instance, destabilizing it by only ~20 meV/atom and without inducing qualitative change in the C local density of states. The CNT was positioned to have one C atom exactly above the strongest H-binding O site of the  $ZnZrO_x$ . Adsorption of a single H atom was studied on the external wall of CNT, because the adsorption of one H on the interior wall is much weaker (Gibbs adsorption energy of 2.28 eV) due to the formation of unstable distorted walls.<sup>11</sup> For the fully hydrogenated CNT(5,5), the H atoms alternate binding on the inner and outer walls, and the length of the lattice vector along the tube length for the unit cell (20 C and 20 H atoms) was expanded from the 2.46 Å to 2.55 Å to minimize the energy of the system. The strain from lattice mismatch with the oxide was minimized to -1.57 % by combining 5 unit cells of the hydrogenated CNT with the ZnZrO<sub>x</sub>(101) supercell scaled by the [(1,1),(0,2)] transformation matrix.

# 2. Supplementary tables and figures

| Catalyst                                | Surface<br>Zn/(Zn+Zr)% <sup>a</sup> | $S_{\rm BET}{}^{\rm b}$ (m <sup>2</sup> g <sup>-1</sup> ) | Pd wt% in<br>total catalyst | Pd:ZnZrO <sub>x</sub><br>mass ratio | $D_{\mathrm{Pd}}^{\mathrm{c}}(\%)$ |
|---|-------------------------------------|---|-----------------------------|-------------------------------------|------------------------------------|
| ZnZrO <sub>x</sub>                      | 20.8                                | 42  | none                        | none                                | $n.d.^d$ $(n.d.^d)$                |
| $Pd/ZnZrO_x$                            | n.a. <sup>e</sup>                   | 50  | 1                           | 1:99                                | 18 (12)                            |
| Pd/CNT                                  | none                                | 101   | 2                           | -                                   | 21 (20)                            |
| Pd/CNT+ZnZrO <sub>x</sub>               | n.a. <sup>e</sup>                   | -   | 0.67                        | 1:100                               | 20 (23)                            |
| $CNT+ZnZrO_x$                           | 20.6 <sup>f</sup>                   | -   | none                        | none                                | none                               |
| Pd/GNP                                  | none                                | 711   | 2                           | -                                   | 16                                 |
| Pd/GNP+ZnZrO <sub>x</sub>               | n.a. <sup>e</sup>                   | -   | 0.67                        | 1:100                               | 16                                 |
| Pd/AC                                   | none                                | 539   | 2                           | -                                   | 23                                 |
| $Pd/AC+ZnZrO_x$                         | n.a. <sup>e</sup>                   | -   | 0.67                        | 1:100                               | 22                                 |
| Pd/SiO <sub>2</sub>                     | none                                | 392   | 2                           | -                                   | 18 (19)                            |
| Pd/SiO <sub>2</sub> +ZnZrO <sub>x</sub> | n.a. <sup>e</sup>                   | -   | 0.67                        | 1:100                               | 18                                 |
| Pd/TiO <sub>2</sub>                     | none                                | 52  | 2                           | -                                   | 22 (20)                            |
| Pd/TiO <sub>2</sub> +ZnZrO <sub>x</sub> | n.a. <sup>e</sup>                   | -   | 0.67                        | 1:100                               | 20                                 |

Supplementary Table 1. Structural characterization of catalysts

<sup>a</sup> Measured by XPS.

<sup>b</sup> BET surface area

<sup>c</sup> Dispersion of Pd ( $D_{Pd}$ ) determined by H<sub>2</sub>-chemisorption at 343 K. The values in parenthesis indicate the value obtained from CO-chemisorption at 343 K. <sup>d</sup> Cannot be determined. The chemisorption amount was measured as almost 0.

<sup>e</sup> Not available due to the distortion of Zr signal in the presence of Pd.

<sup>f</sup> The value indicates physical mixing does not affect surface Zn/(Zn+Zr).

**Supplementary Table 2.** GHSV condition and  $CO_2$  hydrogenation result for each catalyst shown in Fig. 2a. The average values and standard deviations were determined by at least three measurements (reaction condition: 533 K, 5 MPa,  $CO_2/H_2/Ar=19/76/5$ ).

| Catalyst                                | GHSV<br>(cm <sup>3</sup> STP g <sub>cat.</sub> <sup>-1</sup> h <sup>-1</sup> ) | CO <sub>2</sub><br>conv.% | MeOH<br>sel.% | CO<br>sel.% | CH4<br>sel.%      | DME<br>sel.%      |
|---|--|---------------------------|---------------|-------------|-------------------|-------------------|
| $ZnZrO_x$                               | 24000  | 0.94±0.09                 | 88±1          | 12±1        | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
| $Pd/ZnZrO_x$                            | 48000  | 1.20±0.07                 | 80±2          | 20±2        | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
| Pd/CNT+ZnZrO <sub>x</sub>               | 144000   | $0.99 \pm 0.04$           | 75±2          | 25±2        | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
| Pd/ZnZrO <sub>x</sub> +CNT              | 90000  | 1.36±0.06                 | 49±2          | 51±2        | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
| $CNT+ZnZrO_x$                           | 24000  | 0.64±0.10                 | 89±1          | 11±1        | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
| Pd/GNP+ZnZrO <sub>x</sub>               | 72000  | 0.96±0.06                 | 80±2          | 20±2        | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
| Pd/AC+ZnZrO <sub>x</sub>                | 72000  | 1.20±0.06                 | 78±3          | 78±3        | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
| Pd/SiO <sub>2</sub> +ZnZrO <sub>x</sub> | 24000  | 1.25±0.18                 | 54±4          | 46±4        | $0.11 \pm 0.04$   | n.d. <sup>a</sup> |
| Pd/TiO <sub>2</sub> +ZnZrO <sub>x</sub> | 96000  | 1.08±0.14                 | 18±1          | 78±1        | 3.40±0.06         | 0.14±0.01         |

<sup>a</sup> Not detected.

| Catalyst                  | Reaction<br>temp. (K) | CO <sub>2</sub><br>conv.% | MeOH<br>sel.% | CO<br>sel.%       | CH4<br>sel.%      | DME<br>sel.%      |
|---------------------------|-----------------------|---------------------------|---------------|-------------------|-------------------|-------------------|
| ZnZrO <sub>x</sub>        | 513                   | 0.28                      | 100           | n.d. <sup>a</sup> | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 533                   | 0.87                      | 87.1          | 12.9              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 553                   | 2.17                      | 83.7          | 16.3              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 573                   | 4.39                      | 85.1          | 14.9              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 593                   | 7.69                      | 83.0          | 16.3              | n.d. <sup>a</sup> | 0.67              |
|                           | 613                   | 11.6                      | 77.3          | 21.7              | n.d. <sup>a</sup> | 1.00              |
|                           | 633                   | 15.4                      | 65.0          | 33.5              | 0.13              | 1.30              |
| Pd/ZnZrO <sub>x</sub>     | 513                   | 0.73                      | 88.1          | 11.9              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 533                   | 2.00                      | 81.7          | 18.3              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 553                   | 4.09                      | 82.9          | 17.1              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 573                   | 7.32                      | 83.9          | 16.1              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 593                   | 11.6                      | 81.5          | 18.5              | 0.02              | n.d. <sup>a</sup> |
|                           | 613                   | 15.4                      | 73.7          | 25.8              | 0.21              | 0.29              |
|                           | 633                   | 17.8                      | 58.1          | 41.1              | 0.30              | 0.41              |
| Pd/CNT+ZnZrO <sub>x</sub> | 513                   | 3.13                      | 81.8          | 18.2              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 533                   | 4.76                      | 79.8          | 20.2              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 553                   | 7.37                      | 76.2          | 23.8              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 573                   | 11.7                      | 72.1          | 27.9              | n.d. <sup>a</sup> | n.d. <sup>a</sup> |
|                           | 593                   | 18.1                      | 66.3          | 33.7              | 0.06              | n.d. <sup>a</sup> |
|                           | 613                   | 22.3                      | 52.3          | 47.4              | 0.19              | 0.20              |

**Supplementary Table 3.** CO<sub>2</sub> hydrogenation results for ZnZrO<sub>x</sub>, Pd/ZnZrO<sub>x</sub>, and Pd/CNT+ZnZrO<sub>x</sub> catalysts. (reaction condition: 5 MPa, CO<sub>2</sub>/H<sub>2</sub>/Ar=19/76/5, GHSV = 24000 cm<sup>3</sup><sub>STP</sub> g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>).

<sup>a</sup> Not detected.

| Catalyst   | Reaction condition   | STY <sub>MeOH</sub>                    | Ref. |  |  |
|--|--|--|------|--|--|
|  |  | $(g \ g_{cat.}{}^{-1} \ h^{-1})^{a,b}$ |      |  |  |
| ZnZrO <sub>x</sub>   | 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 24000 cm <sup>3</sup> <sub>STP</sub> $g_{cat.}^{-1}$ h <sup>-1</sup>                                  | 0.730                                  | 6    |  |  |
| (Coprecipitation)  | Coprecipitation) $315 \text{ °C}, 5.0 \text{ MPa}, \text{H}_2/\text{CO}_2=4, 24000 \text{ cm}^3 _{\text{STP}}  \text{g}_{\text{cat.}^{-1}}  \text{h}^{-1}$ |  |      |  |  |
| ZnZrO <sub>x</sub><br>(EISA process)                           | 320 °C, 5.5 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 24000 cm <sup>3</sup> s <sub>TP</sub> $g_{cat}$ <sup>-1</sup> h <sup>-1</sup>                         | 0.707                                  | 12   |  |  |
| ZnZrO <sub>x</sub><br>(Aerogel synthesis)                      | 340 °C, 4.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 21180 cm <sup>3</sup> sTP $g_{cat.}^{-1}$ h <sup>-1</sup>   | 0.547                                  | 13   |  |  |
| ZnZrO <sub>x</sub><br>(Coprecipitation with<br>micro-reactor)  | 320 °C, 3.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 12000 cm <sup>3</sup> stp $g_{cat}$ <sup>-1</sup> h <sup>-1</sup>                                     | 0.350                                  | 14   |  |  |
| 0.8 at.% Pd-ZnZrO <sub><math>x</math></sub> (coprecipitation)  | 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 24000 cm <sup>3</sup> <sub>STP</sub> $g_{cat}$ <sup>-1</sup> h <sup>-1</sup>                          | 0.630 (0.710) <sup>c</sup>             | 15   |  |  |
| 0.1 wt% Pd-ZnZrO <sub><math>x</math></sub> (coprecipitation)   | 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 30000 cm <sup>3</sup> <sub>STP</sub> $g_{cat.}^{-1}$ h <sup>-1</sup>                                  | 0.735                                  | 16   |  |  |
| 0.5 at.% Cu-ZnZrO <sub><math>x</math></sub> (coprecipitation)  | 310 °C, 4.5 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 10800 cm <sup>3</sup> sTP $g_{cat.}^{-1}$ h <sup>-1</sup>   | 0.300                                  |      |  |  |
| 0.02 at.% Pd-ZnZrO <sub>x</sub> (coprecipitation)              | 320 °C, 4.5 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 10800 cm <sup>3</sup> sTP g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                              | 0.303                                  | 17   |  |  |
| 0.02 at.% Pt-ZnZrO <sub><math>x</math></sub> (coprecipitation) |  | 0.290                                  |      |  |  |
| ZnZrO <sub>x</sub>   |  | 0.430                                  | This |  |  |
| $Pd/CNT+ZnZrO_x$<br>(physical mixing)                          | <sup>-</sup> 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 24000 cm <sup>3</sup> <sub>STP</sub> $g_{cat}$ <sup>-1</sup> h <sup>-1</sup>             | 0.900 <sup>d</sup>                     | work |  |  |

**Supplementary Table 4.** Summary of the catalytic performances of  $CO_2$  hydrogenation to methanol over  $ZnZrO_x$  and metal-promoted  $ZnZrO_x$  catalysts.

<sup>a</sup> If it is not shown in the literature, the value was estimated by using  $CO_2$  conversion, methanol selectivity, space velocity, and concentration of  $CO_2$  in the reactant gas mixture.

<sup>d</sup> The value in parenthesis indicates the  $STY_{MeOH}$  after 600 h reaction.

<sup>&</sup>lt;sup>b</sup> As some literature reported dimethyl ether (DME) as the secondary product from methanol (MeOH) condensation, the DME production rate was also included under the assumption '1 DME = 2 MeOH'. <sup>c</sup> The value in parenthesis indicates the STY<sub>MeOH</sub> after 100 h reaction.

| Catalysts  | Reaction conditions   | TOS (h)           | $\frac{\text{STY}_{\text{MeOH}}}{(\text{g g}_{\text{cat.}}^{-1}\text{h}^{-1})}$ | Ref.      |
|--|---|-------------------|---|-----------|
| Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>                 | 250 °C, 3.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 30000 cm <sup>3</sup> stp g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>             | 600               | 0.85  | 18        |
| Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>                              | 300 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 20000 cm <sup>3</sup> <sub>STP</sub> $g_{cat}$ <sup>-1</sup> $h^{-1}$                | 100               | 0.122   | 19        |
| Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>                 | 260 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 24000 cm <sup>3</sup> stp $g_{cat}$ <sup>-1</sup> h <sup>-1</sup>                    | 600               | 0.627   | This work |
| Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>                 | 200 °C, 3.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 9000 cm <sup>3</sup> <sub>STP</sub> $g_{cat}^{-1}$ h <sup>-1</sup>                   | 720               | 0.119   | 20        |
| Cu/ZnO/ZrO2  | 220 °C, 3.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 6000 cm <sup>3</sup> <sub>STP</sub> $g_{cat}$ <sup>-1</sup> h <sup>-1</sup>          | 16                | 0.297   | 21        |
| Cu/ZnO/5Ga   | 240 °C, 4.5 MPa, H <sub>2</sub> /CO <sub>2</sub> =2.8, 18000 cm <sup>3</sup> <sub>STP</sub> $g_{cat.}^{-1}$ h <sup>-1</sup>               | n.s. <sup>b</sup> | 0.880   | 22        |
| 3DOM-Cu/ZnO/ZrO <sub>2</sub>                                       | 240 °C, 4.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 18000 cm <sup>3</sup> stp g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>             | 16                | 0.747   | 23        |
| ZnZrO <sub>x</sub>   | 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 24000 cm <sup>3</sup> stp g <sub>cat.</sub> <sup>-1</sup> h <sup>-1</sup>            | 500               | 0.730   | 6         |
| ZnZrO <sub>x</sub>   | 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 24000 cm <sup>3</sup> <sub>STP</sub> $g_{cat.}^{-1}$ h <sup>-1</sup>                 | 150               | 0.430   | This work |
| Pd/CNT+ZnZrO <sub>x</sub>  | 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 24000 cm <sup>3</sup> <sub>STP</sub> g <sub>cat.</sub> <sup>-1</sup> h <sup>-1</sup> | 600               | 0.900 (1.351) <sup>c</sup>  | This work |
| c-In <sub>2</sub> O <sub>3</sub> -S                                | 300 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 9000 cm <sup>3</sup> <sub>STP</sub> $g_{cat}^{-1} h^{-1}$                            | 130               | 0.34  | 24        |
| In <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>                   | 300 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 16000 cm <sup>3</sup> stp g <sub>cat.</sub> <sup>-1</sup> h <sup>-1</sup>            | 1000              | 0.30  | 19        |
| $CdZrO_x$  | 300 °C, 2.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 24000 cm <sup>3</sup> stp g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>             | 3                 | 0.358   | 25        |
| GaZnZrO <sub>x</sub>   | 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 24000 cm <sup>3</sup> <sub>STP</sub> g <sub>cat.</sub> <sup>-1</sup> h <sup>-1</sup> | 100               | 0.630   | 26        |
| Pd/In <sub>2</sub> O <sub>3</sub>                                  | 280 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 24000 cm <sup>3</sup> stp g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>             | 90                | 0.61  | 27        |
| Pd/In <sub>2</sub> O <sub>3</sub>                                  | 300 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 21000 cm <sup>3</sup> stp g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>             | n.s. <sup>b</sup> | 0.885   | 28        |
| Ir/In <sub>2</sub> O <sub>3</sub>                                  | 300 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 21000 cm <sup>3</sup> stp g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>             | 12                | 0.75  | 29        |
| Au/In <sub>2</sub> O <sub>3</sub>                                  | 300 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 21000 cm <sup>3</sup> stp g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>             | 12                | 0.47  | 30        |
| Pt/In <sub>2</sub> O <sub>3</sub>                                  | 300 °C, 4.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 24000 cm <sup>3</sup> <sub>STP</sub> g <sub>cat.</sub> <sup>-1</sup> h <sup>-1</sup> | n.s. <sup>b</sup> | 0.475   | 31        |
| InNi <sub>3</sub> C <sub>0.5</sub> /m-ZrO <sub>2</sub>             | 300 °C, 4.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 24000 cm <sup>3</sup> stp g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>             | 120               | 0.62  | 32        |
| InNi <sub>3</sub> C <sub>0.5</sub> /Fe <sub>3</sub> O <sub>4</sub> | 320 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3, 24000 cm <sup>3</sup> stp g <sub>cat.</sub> <sup>-1</sup> h <sup>-1</sup>            | 500               | 1.01  | 32        |
| In@Co  | 300 °C, 5.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =4, 27500 cm <sup>3</sup> <sub>STP</sub> $g_{cat.}^{-1}$ h <sup>-1</sup>                 | 90                | 0.86  | 33        |

| Supplementary | Table 5. | Comparison | of state-of-th | ne-art catalys | sts in CO <sub>2</sub> | hydrogenation | to methanol. |
|---------------|----------|------------|----------------|----------------|------------------------|---------------|--------------|
|               |          |            |                |                |                        |               |              |

<sup>a</sup> Denotes a commercial catalyst.
<sup>b</sup> Not shown in the literature.
<sup>c</sup> Number in parenthesis is the normalized to the active phase (ZnZrO<sub>x</sub>).



**Supplementary Figure 1. a** High-magnification TEM image, **b** low-magnification TEM image, and **c** SEM image of  $ZnZrO_x$ .



Supplementary Figure 2. a TEM image and b Pd particle size distribution of Pd/CNT.



**Supplementary Figure 3.** (**a**, **c**, **e**, **g**) TEM images and (**b**, **d**, **f**, **h**) Pd particle size distributions of Pd/*support* catalysts. (**a**, **b**) Pd/GNP, (**c**, **d**) Pd/AC, (**e**, **f**) Pd/SiO<sub>2</sub>, (**g**, **h**) Pd/TiO<sub>2</sub>.



**Supplementary Figure 4.** Powder XRD patterns of Pd/GNP+ZnZrO<sub>x</sub>, Pd/AC+ZnZrO<sub>x</sub>, Pd/SiO<sub>2</sub>+ZnZrO<sub>x</sub>, and Pd/TiO<sub>2</sub>+ZnZrO<sub>x</sub>.



**Supplementary Figure 5. a** MeOH formation rates, and **b** CO formation rates of standalone Pd/*support* catalysts. The results for ZnZrO<sub>x</sub> are included for comparison (533 K, 5 MPa, CO<sub>2</sub>/H<sub>2</sub>/Ar=19/76/5, GHSV 24000 cm<sup>3</sup><sub>STP</sub>  $g_{cat.}^{-1}$  h<sup>-1</sup> for ZnZrO<sub>x</sub>, GHSV 48000 cm<sup>3</sup><sub>STP</sub>  $g_{cat.}^{-1}$  h<sup>-1</sup> for Pd/*support* catalysts).



**Supplementary Figure 6.** Reaction order analysis for **a** H<sub>2</sub>, and **b** CO<sub>2</sub> of the catalysts (Condition: 533 K and 5 MPa. GHSVs are shown in Supplementary Table 2). For figure a,  $P(H_2)$  were controlled from 2.6 to 4.1 MPa under a fixed  $P(CO_2) = 0.65$  MPa. For figure b,  $P(CO_2)$  were controlled from 0.5 to 0.95 MPa under a fixed  $P(H_2) = 3.8$  MPa.



**Supplementary Figure 7.** Arrhenius plot for determination of the apparent activation energy ( $E_a$ ) of the catalysts. (Condition: 493–553 K, 5 MPa, and CO<sub>2</sub>/H<sub>2</sub>/Ar = 19/76/5. GHSVs are shown in Supplementary Table 2)



**Supplementary Figure 8.** Methanol selectivity of  $ZnZrO_x$ ,  $Pd/ZnZrO_x$ , and  $Pd/CNT+ZnZrO_x$  catalysts as a function of CO<sub>2</sub> conversion in the range of 0.7–18% (Condition: 513–633 K, 5 MPa, CO<sub>2</sub>/H<sub>2</sub>/Ar = 19/76/5, GHSV = 24000 cm<sup>3</sup> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>).



**Supplementary Figure 9. Catalytic performance of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts. a** Methanol yield and STY<sub>MeOH</sub> of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts as a function of reaction temperature. The dashed line indicates the methanol yield at thermodynamic equilibrium. Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts commonly show the highest methanol yield at *ca*. 533 K. **b** Long-term catalytic test result of lab-made Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst at 533 K. The result supports that a rapid deactivation is the general behavior of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>.



**Supplementary Figure 10.** Zn K edge XAFS analysis of the catalysts. a Zn K edge XANES of the ZnZrO<sub>x</sub> and Pd/CNT+ZnZrO<sub>x</sub> catalysts before and after reaction. The used catalysts were obtained after the reaction shown in Fig. 3b. **b** Normalized absorbance of edge as a function of  $E_0$  for catalysts as well as standard Zn compounds. Except for ZnO (experimental), the values for standard Zn compounds were adopted from ref.<sup>34</sup>. The result indicates that Zn in ZnZrO<sub>x</sub> exists as the intermediate state between tetrahedral and octahedral structure, proving that the solid solution structure of which Zn is highly dispersed in the ZrO<sub>2</sub> domain. **c** Zn K edge  $k^3$ -weighted Fourier transforms of the EXAFS of the ZnZrO<sub>x</sub> and Pd/CNT+ZnZrO<sub>x</sub> catalysts before and after reaction. The overall results represent that Zn is not changed during the long-term reaction.



**Supplementary Figure 11. Zr K edge XAFS analysis of the catalysts. a** Zr *K* edge XANES of the ZnZrO<sub>x</sub> and Pd/CNT+ZnZrO<sub>x</sub> catalysts before and after reaction. The used catalysts were obtained after the reaction shown in Fig. 3b. b Zr *K* edge  $k^3$ -weighted Fourier transforms of the EXAFS of the ZnZrO<sub>x</sub> and Pd/CNT+ZnZrO<sub>x</sub> catalysts before and after reaction. The overall results represent that Zr is not changed during the long-term reaction.



**Supplementary Figure 12.** Long-term catalytic tests of Pd/CNT+ZnZrO<sub>x</sub> at 593 K, and commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at 533 K (Condition: 5 MPa, CO<sub>2</sub>/H<sub>2</sub>/Ar = 19/76/5, GHSV = 80000 cm<sup>3</sup><sub>STP</sub> g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>). The test was measured far below the thermodynamic equilibrium.



**Supplementary Figure 13.** CO<sub>2</sub>-TPD profiles of ZnZrO<sub>x</sub>, Pd/ZnZrO<sub>x</sub>, and Pd/CNT+ZnZrO<sub>x</sub>. Three catalysts show a similar CO<sub>2</sub> adsorption strength distribution. Pd/ZnZrO<sub>x</sub> shows a 21% higher CO<sub>2</sub> adsorption capacity (0.987 mmol  $g_{ZnZrOx}^{-1}$ ) than ZnZrO<sub>x</sub> (0.814 mmol  $g_{ZnZrOx}^{-1}$ ). This is coherent with their surface area gap (20%, Supplementary Table 1). Pd/CNT+ZnZrO<sub>x</sub> shows almost the same adsorption capacity (0.803 mmol  $g_{ZnZrOx}^{-1}$ ) compared to ZnZrO<sub>x</sub>,



Supplementary Figure 14. H<sub>2</sub>-TPD profiles of Pd/SiO<sub>2</sub>, Pd/SiO<sub>2</sub>+ZnZrO<sub>x</sub>, Pd/TiO<sub>2</sub>, and Pd/TiO<sub>2</sub>+ZnZrO<sub>x</sub>. The amount of reversible H<sub>2</sub> (quantified in the range of 323–533 K) on the catalysts were determined as follows. Pd/SiO<sub>2</sub> = 7.9 µmol  $g_{cat}^{-1}$ , Pd/SiO<sub>2</sub>+ZnZrO<sub>x</sub> = 9.8 µmol  $g_{cat}^{-1}$ , Pd/TiO<sub>2</sub> = 20.7 µmol  $g_{cat}^{-1}$ , and Pd/TiO<sub>2</sub>+ZnZrO<sub>x</sub> = 16.4 µmol  $g_{cat}^{-1}$ .



Supplementary Figure 15. Tauc plot of UV-Vis-NIR spectra and bandgap determination for support materials.



**Supplementary Figure 16.** Zn 2*p* XPS of a ZnZrO<sub>*x*</sub>, and b Pd/CNT+ZnZrO<sub>*x*</sub> catalysts before and after sequential gas treatments (without sample exposure to air; gas treatment condition:  $H_2$  at 673 K, CO<sub>2</sub> at 533 K, CO<sub>2</sub>+H<sub>2</sub> (1:4) at 533 K).



**Supplementary Figure 17.** Zr 3*d* XPS of **a** ZnZrO<sub>*x*</sub>, and **b** Pd/CNT+ZnZrO<sub>*x*</sub> catalysts before and after sequential gas treatments (without sample exposure to air; gas treatment condition:  $H_2$  at 673 K, CO<sub>2</sub> at 533 K, CO<sub>2</sub>+H<sub>2</sub> (1:4) at 533 K).



**Supplementary Figure 18.** O 1*s* XPS of **a** ZnZrO<sub>*x*</sub>, and **b** Pd/CNT+ZnZrO<sub>*x*</sub> catalysts before and after sequential gas treatments (without sample exposure to air; gas treatment condition:  $H_2$  at 673 K, CO<sub>2</sub> at 533 K, CO<sub>2</sub>+H<sub>2</sub> (1:4) at 533 K).



**Supplementary Figure 19.** C 1*s* XPS of Pd/CNT+ZnZrO<sub>*x*</sub> catalysts before and after sequential gas treatments (without sample exposure to air; gas treatment condition:  $H_2$  at 673 K, CO<sub>2</sub> at 533 K, CO<sub>2</sub>+H<sub>2</sub> (1:4) at 533 K).



**Supplementary Figure 20.** Pd 3*d* (and Zr 3*p*) XPS of Pd/CNT+ZnZrO<sub>*x*</sub> catalysts before and after sequential gas treatments (without sample exposure to air; gas treatment condition:  $H_2$  at 673 K, CO<sub>2</sub> at 533 K, CO<sub>2</sub>+H<sub>2</sub> (1:4) at 533 K).



Supplementary Figure 21. Relative DFT energies ( $E_{rel}$ ) of  $Zn_2Zr_{n-2}O_{2n-2}$  structure with two O vacancies per unit cell of a model with Zn–Zn distance of 7.296 Å, formed via substitution of two Zn atoms to Zr to acquire the Zn to Zr concentration on surface in 1:4 ratio. Second O vacancy is generated near Zn atom with respect to first O vacancy highlighted as "Vac" positions in these structures. Note that O vacancies are created near Zn atoms.



Supplementary Figure 22. Relative DFT energies ( $E_{rel}$ ) of  $Zn_2Zr_{n-2}O_{2n-2}$  structure with two O vacancies per unit cell of a model with Zn–Zn distance of 6.275 Å, formed via substitution of two Zn atoms to Zr atoms to acquire 1:4 Zn to Zr concentration on the surface. The second O vacancy is generated near Zn atom with respect to first O vacancy highlighted as "Vac" positions in these structures. Note that O vacancies are created near Zn atoms.



Supplementary Figure 23. Oxygen vacancy formation energy for the third vacancy per unit cell. Different O positions including top and subsurface atoms were removed to generate  $Zn_2Zr_{n-2}O_{2n-3}$  model.



Supplementary Figure 24. Oxygen vacancy formation energy for the third vacancy per unit cell in the presence of H atoms adsorbed on the surface. Different O positions including top and subsurface atoms were removed to scan the  $Zn_2Zr_{n-2}O_{2n-3}H_4$  surface. In these calculations O atoms bound to surface H were removed as OH groups.



**Supplementary Figure 25. DFT adsorption energy of hydrogen on**  $Zn_2Zr_{n-2}O_{2n-2}$  **surface. a** Adsorption of a single H atom. **b** Dissociative adsorption of H<sub>2</sub>, and **c** adsorption of the fourth H atom produced by dissociative adsorption of the second H<sub>2</sub> molecule on  $Zn_2Zr_{n-2}O_{2n-2}$  (101) surface. Homolytic dissociative adsorption of H<sub>2</sub> molecule on 2 O atoms near Zn atom with DFT energy of 0.08 eV is illustrated by the hexagon in figure **c**.



**Supplementary Figure 26. Structure of Pd<sub>127</sub> nanoparticles on graphene.** Binding energies of Pd<sub>127</sub> particles on graphene at different adsorption sites with different rotation angles around the normal to graphene passing through the center of mass of the particle,  $E_b = E[Pd/graphene] - E[graphene] - E[Pd]$ . Images on the left illustrate centering of the center of mass of Pd nanoparticle at **a** top, **b** bridge, and **c** hollow C sites corresponding to 0 degrees (Grey: C and turquoise: Pd). The most stable structure considered in further studies is highlighted by the red rectangle.



Supplementary Figure 27. Reaction data for commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst (CZA) versus Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> physically mixed with CNT (CZA+CNT, CZA:CNT = 2:1 mass ratio). a CO<sub>2</sub> conversion, b MeOH selectivity, and c  $r_{MeOH}$  (mmol  $g_{CZA}^{-1}$  h<sup>-1</sup>) as a function of reaction pressure.

## 3. Identify kinetics-controlled region

We tested CO<sub>2</sub> hydrogenation over ZnZrO<sub>x</sub> catalyst by varying GHSV under fixed temperature (533 K), pressure (5 MPa), and feed composition (CO<sub>2</sub>/H<sub>2</sub>/Ar = 19/76/5). The CO<sub>2</sub> consumption rate (mmol g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>) is consistent under the condition where GHSV  $\geq$  18000 cm<sup>3</sup><sub>STP</sub> g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup> (Supplementary Fig. 28b). When plotting the reaction rate as a function of CO<sub>2</sub> conversion, the corresponding region is CO<sub>2</sub> conversion  $\leq$  1.5% (Supplementary Fig. 28c), although when CO<sub>2</sub> conversion falls below 0.5% experimental error is large (i.e. carbon balance < 90%). Consequently, the activity of catalysts was determined in the conversion range of 0.5–1.4% region (see Supplementary Table 2). This conversion level is far below the thermodynamic equilibrium CO<sub>2</sub>-to-MeOH conversion at the given condition (533 K, 5 MPa, H<sub>2</sub>/CO<sub>2</sub> = 4, *ca.* 24%).



Supplementary Figure 28. Identify kinetics-controlled region for  $ZnZrO_x$ . a CO<sub>2</sub> conversion as a function of 1/GHSV. b CO<sub>2</sub> consumption rate as a function of GHSV. c CO<sub>2</sub> consumption rate as a function of CO<sub>2</sub> conversion (Condition: 533 K, 5 MPa, CO<sub>2</sub>/H<sub>2</sub>/Ar = 19/76/5).

The effect of external diffusion was tested by simultaneously varying the flow rate and catalyst mass in a fixed GHSV for three catalysts, i.e.  $ZnZrO_x$ ,  $Pd/ZnZrO_x$ , and  $Pd/CNT+ZnZrO_x$ .  $ZnZrO_x$  and  $Pd/ZnZrO_x$  show consistent  $r_{MeOH}$  regardless of flow rate and catalyst mass, demonstrating under the testing condition (flow rate  $\ge 20 \text{ cm}^3_{\text{STP}}$  min<sup>-1</sup> and catalyst mass  $\ge 0.05 \text{ g}$ ) the system is not limited by the external mass transfer (Supplementary Fig. 29a,b). Pd/CNT+ZnZrO\_x shows a gradual increase of  $r_{MeOH}$  under low flow condition (flow rate  $\le 96 \text{ cm}^3_{\text{STP}} \text{ min}^{-1}$  and catalyst mass  $\le 0.04 \text{ g}$ ), but exhibits consistent  $r_{MeOH}$  at higher flow rate and more amount of catalyst mass

condition (Supplementary Fig. 29c). Therefore, we used 0.05 g of catalyst and 120 cm<sup>3</sup><sub>STP</sub> min<sup>-1</sup> of flow rate to test Pd/CNT+ZnZrO<sub>x</sub>.

We also compared the effect of internal diffusion for three catalysts,  $ZnZrO_x$ ,  $Pd/ZnZrO_x$ , and  $Pd/CNT+ZnZrO_x$ , by varying pellet sizes (180–450 µm v.s. 450–850 µm). All catalysts show consistent  $r_{MeOH}$ , thus the internal diffusion limitation can be ignored in the given pellet sizes (Supplementary Fig. 30).



**Supplementary Figure 29. Evaluation of external mass transfer limitation.** The effect of flow rate and catalyst mass in a fixed GHSV on the reaction rate ( $r_{MeOH}$ ) of **a** ZnZrO<sub>x</sub>, **b** Pd/ZnZrO<sub>x</sub>, and **c** Pd/CNT+ZnZrO<sub>x</sub> (533 K, 5 MPa, CO<sub>2</sub>/H<sub>2</sub>/Ar=19/76/5).



Supplementary Figure 30. Evaluation of the internal mass transfer limitation. The effect of pellet sizes on the activity of  $ZnZrO_x$ ,  $Pd/ZnZrO_x$ , and  $Pd/CNT+ZnZrO_x$  (533 K, 5 MPa,  $CO_2/H_2/Ar=19/76/5$ , GHSVs are shown in Supplementary Table 2).

# 4. Estimation of interfacial area of Pd and ZnZrO<sub>x</sub> in Pd/ZnZrO<sub>x</sub>

To estimate the interfacial area of Pd with  $ZnZrO_x$  in Pd/ZnZrO<sub>x</sub>, we assumed that semispherical Pd particles of face-centered cubic structure (atomic packing factor = 0.74) and diameters of 5 nm are uniformly dispersed on the surface of  $ZnZrO_x$  (1 wt% of Pd in the catalyst, Supplementary Table 1).  $N_{Pd, 5nm}$  which represents the number of Pd atoms in a 5 nm cluster can be obtained as follows:

$$N_{\rm Pd, 5 nm} = 0.5 \times \frac{V_{5 nm}}{V_{atom}} = 0.5 \times \frac{0.74 \times \frac{1}{6}\pi (d_{5 nm})^3}{\frac{1}{6}\pi (d_{atom})^3} = 0.5 \times \frac{0.74 \times \frac{1}{6}\pi (5 nm)^3}{\frac{1}{6}\pi (0.274 nm)^3} = 2248 \text{ (atoms)}$$
(15)

In turn,  $A_{Pd, 5 nm}$  which represents the contact area of a single 5 nm Pd particle with support can be obtained as follows:

$$A_{\rm Pd, 5 nm} = \pi r^2 = \pi (\frac{d}{2})^2 = \pi (2.5 \text{ nm})^2 = 19.6 \text{ nm}^2$$
(16)

Finally, the interfacial area between Pd particles and  $ZnZrO_x$  can be obtained by the following equation:

Interfacial area 
$$= \frac{N_{Pd, total}}{N_{Pd, 5 nm}} \times A_{Pd, 5 nm} = \frac{0.01 \, g_{Pd} \, g_{cat.}^{-1} \times 106.42^{-1} \, mol \, g_{Pd}^{-1} \times N_A \, atoms \, mol^{-1}}{2248 \, atoms} \times 19.6 \, nm^2,$$
 (17)

where  $N_A$  means Avogadro number.

The interfacial area is estimated to be 0.49 m<sup>2</sup> g<sup>-1</sup>. This is about 1% of the surface area of the catalyst (50 m<sup>2</sup> g<sup>-1</sup>, Supplementary Table 1).

## 5. Effects of mortar grinding on ZnZrO<sub>x</sub>

In order to check the effect of mortar grinding on  $ZnZrO_x$ , we compared BET surface area and catalytic activity of unground  $ZnZrO_x$  and mortar ground  $ZnZrO_x$  (i.e. a standard catalyst in the study). As  $ZnZrO_x$  is intrinsically a lump, the catalyst was just sieved without any physical grinding and pelletizing during the preparation step of catalytic reaction. As shown in Supplementary Fig. 31, mortar grinding slightly reduces surface area from 44 to 42 m<sup>2</sup> g<sup>-1</sup>, thus it is not beneficial for improving gas diffusion to the active site of  $ZnZrO_x$ . Two catalysts also show identical activity within the error range.



**Supplementary Figure 31. Effects of mortar grinding on ZnZrO**<sub>*x*</sub>. (a) BET surface area and (b) methanol formation activity of unground and mortar ground ZnZrO<sub>*x*</sub> catalysts (Condition: 533 K, 5 MPa, and CO<sub>2</sub>/H<sub>2</sub>/Ar = 19/76/5, GHSV = 24000 cm<sup>3</sup><sub>STP</sub> g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>).

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