

Support-dependent rate-determining step of CO₂ hydrogenation to formic acid on metal oxide supported Pd catalysts

Zhenhua Zhang^a, Liyuan Zhang^b, Siyu Yao^c, Xiaozhe Song^a, Weixin Huang^b, Max J.

Hülsey^{*,a}, Ning Yan^{*,a}

^a Department of Chemical and Biomolecular Engineering, National University of Singapore,

Blk E5, 4 Engineering Drive 4, Singapore 117585

^b Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials for Energy Conversion and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, P. R. China

^c Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, United

States

*To whom correspondence should be addressed. E-mail: m.huelsey@u.nus.edu,

ning.yan@nus.edu.sg

Experimental details

Preparation of Pd/ZnO catalysts. Various Pd loadings of Pd/ZnO catalysts were synthesized by the similar procedures with Pd/CeO₂ catalysts. Typically, an aqueous solution of 1 mol L⁻¹ Na₂CO₃ was added dropwise to an aqueous mixture (100 mL) of PdCl₂ with different contents and zinc nitrate hexahydrate (7.3 g L⁻¹) at 323 K until the pH value reached 10 with the stirring rate of 600 r/min. The mixed solution was kept for 3 h under continuous stirring. The resulting precipitate was acquired by centrifugation, and then washed with deionized water until no Cl⁻ can be detected. The acquired solids were dried at oven at 333 K for 12 h, then calcined in air at 623 K for 2 h, and eventually reduced in 5% H₂/N₂ with a flow rate of 30 mL min⁻¹ at 473 K for 1 h. We changed the volumes of added PdCl₂ aqueous solution to change the amounts of added PdCl₂. The acquired catalysts were denoted as x%Pd/ZnO (x is the calculated Pd:ZnO weight ratios).

Preparation of Pd/TiO₂ catalysts. An aqueous solution of PdCl₂ was added into an aqueous dispersion of commercial TiO₂ (P25, 500 mg) at 323 K and the pH was adjusted to 10 by the addition of 1 mol L⁻¹ Na₂CO₃ solution under stirring (600 rpm). The reaction mixture was stirred for 3 hours at 323 K upon which the solid was separated by centrifugation, washed with deionized water until the washing solution did not contain Cl⁻. The obtained solid was then dried for 12 h at 333 K, calcined in air at 623 K for 2 h and reduced in 5% H₂/N₂ with a flow rate of 30 mL min⁻¹ at 473 K for 1 h.

Characterization of catalysts

Inductively coupled plasma optical emission spectrometer (ICP-OES). The Pd loadings in the reduced catalysts were determined using an iCAP 6000 series ICP-OES spectrometer. The reduced catalysts were dissolved in aqua regia (HCl/HNO₃ = 3:1) at room temperature overnight and then diluted with deionized water to a desired volume before analysis.

X-ray diffraction (XRD). Powder XRD patterns were acquired on a Philips X'Pert PROS diffractometer using a nickel-filtered Cu K α (wavelength: 0.15418 nm) radiation source with the operation voltage being 40 kV and operation current being 50 mA. The reduced powder catalysts were firstly pressed into a small tablet before analysis.

X-ray photoelectron spectroscopy (XPS). XPS spectra were acquired on an ESCALAB 250 high performance electron spectrometer using monochromatized Al K α (hv=1486.7 eV) as the excitation source. The reduced samples were stuck on the stage and tested directly. The binding energy of samples was corrected by setting the adventitious carbon (C1s) to 284.8 eV.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The microscopic structure of samples was performed on a JEM 2100F (JEOL, Japan) high resolution transmission electron microscope. The operation voltage was 200 kV. The reduced samples were dispersed in ethanol and then placed on an extra-thick copper grid for analysis.

Surface area determination by *Brunauer-Emmett-Teller (BET)* analysis. BET surface areas were measured using Micromeritics Tristar II 3020M. The pure supports and reduced Pd-based catalysts were degassed at 423 K for 5 h in a N₂ atmosphere prior to the measurement.

X-ray absorption spectroscopy (XAS). The XAFS spectra of the catalysts were collected at the 8-ID beamline of the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory (BNL). For measurement, the reduced samples were pressed into around 1 mm thick pellets (1cm diameter). The Pd L_{III}-edge XAFS spectra were collected in the fluorescence mode using a passivated implanted planar silicon (PIPS) detector. Each reduced sample was measured for 12 times. All parallel measurements were merged into a single spectrum. The data pretreatment and EXAFS fitting were performed using the Ifeffit package.

H₂-temperature programmed reduction (H₂-TPR) and CO₂-temperature programmed desorption (CO₂-TPD). H₂-TPR and CO₂-TPD experiments were performed on

Micromeritics Autochem 2920 apparatus equipped with a TCD detector. In the H₂-TPR experiment, 20 mg as-synthesized fresh catalyst without reduction was put into a quartz reactor and heated at an increasing rate of 5 K/min in 5% H₂ balanced with Ar at a flow rate of 30 mL/min. In the CO₂-TPD experiment, 100 mg fresh catalyst without reduction was first reduced by 5% H₂ balanced with N₂ (30 mL/min) at 473 K for 1 h. Then the flow was switched to pure Ar (30 mL/min), heated to 673 K for 1 h, before cooling down to room temperature in Ar atmosphere. The acquired catalyst was treated in pure CO₂ flow (50 mL/min) for 2 h and purged by Ar (30 mL/min) for 30 min at room temperature. Finally, the catalyst was heated (5 K/min) in pure Ar (30 mL/min) until the temperature reached 600 K, during which the signals were recorded by the TCD detector.

In situ diffuse reflectance infrared Fourier transformed spectra (DRIFTS). *In situ* DRIFTS experiments were performed on a Nicolet iS50 FT-IR spectrometer equipped with a high temperature DRIFTS reaction cell (Harrick Scientific Products, INC) using an MCT/A detector in the series mode with 64 scans and at a resolution of 4 cm⁻¹. For *in situ* DRIFTS of CO adsorption experiments, 50 mg as-synthesized sample without reduction was loaded on the sample stage and heated in 5% H₂ balanced with N₂ (30 mL/min) to 473 K (5 K/min). It was kept at this temperature for 1 h, then the gas flow was switched to pure N₂ (30 mL/min) for another 30 min and finally the system was cooled down to room temperature in N₂ atmosphere. After taking the background spectrum under N₂ atmosphere at room temperature, 5% CO balance with N₂ (50 mL/min) was admitted for 1 h, and then purged with N₂ (30 mL/min). The DRIFTS spectra were recorded during the N₂ purge. For *in situ* DRIFTS of CO₂ + H₂ experiments, the catalyst was first reduced by 5% H₂/N₂ at 473 K following the same procedure as described above. After taking the background spectrum under N₂ atmosphere (30 mL/min) at 373 K, the gas flow was switched into a mixture of CO₂ + H₂ (1:1, 30 mL/min) and the DRIFTS spectra were continuously recorded. For *in situ* DRIFTS of CO₂

and H₂ stepwise experiments, the catalyst was reduced following the same procedure as described above, then treated by pure H₂ (30 mL/min) at 373 K for 1 h. The N₂ flow was switched on (30 mL/min) at the same temperature to take the background spectrum. Next, CO₂ was admitted into the cell (30 mL/min) and the DRIFT spectra were continuously recorded for 1 h. Afterwards, the reaction cell was purged by N₂ (30 mL/min) for 30 min. Finally, H₂ was admitted into the cell again (30 mL/min), while the DRIFTS spectra were recorded continuously for 1 h. The system was maintained at 373 K for the entire measurement.

Catalytic evaluation

For kinetic study, the effect of stirring speed was determined in the range of 400-1200 r/min using 2%Pd/CeO₂ catalyst. The test procedures were same with that of performance evaluation. No difference in production rate was observed at 800 r/min and above, and thus, 800 r/min was selected as the stirring speed for further kinetic studies. The conversions were always controlled below 10 %. The apparent activation energy on 0.05%Pd/CeO₂, 2%Pd/CeO₂, 0.05%Pd/ZnO, 2%Pd/ZnO, and 2%Pd/TiO₂ catalysts were measured in the temperature range of 298 K to 373 K. The reaction order of H₂ was acquired by keeping the sodium bicarbonate mass as 168 mg but varying the H₂ pressure from 1.5 MPa to 2.2 MPa. The reaction order of sodium bicarbonate was acquired by keeping the H₂ pressure at 2 MPa but varying the sodium bicarbonate mass from 33.6 mg to 84 mg.

Table S1. Pd loading (weight %) of different Pd/CeO₂ and Pd/ZnO catalysts determined by OES-ICP.

| Catalysts | Pd loading / wt. % | Catalysts | Pd loading / wt. % |
|--------------------------|--------------------|-------------|--------------------|
| 0.05%Pd/CeO ₂ | 0.049 | 0.05%Pd/ZnO | 0.049 |
| 0.1%Pd/CeO ₂ | 0.12 | 0.1%Pd/ZnO | 0.11 |
| 0.2%Pd/CeO ₂ | 0.23 | 0.2%Pd/ZnO | 0.21 |
| 2%Pd/CeO ₂ | 1.98 | 2%Pd/ZnO | 1.99 |

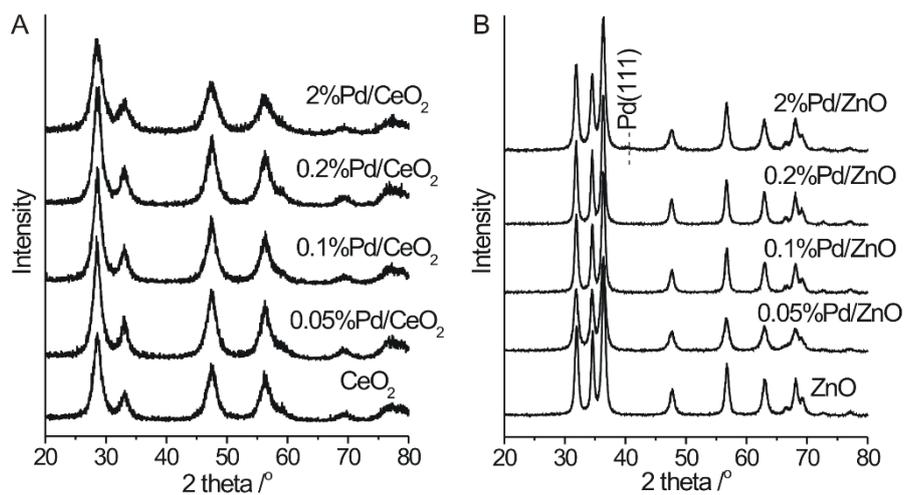


Figure S1. XRD patterns of (A) CeO₂ and various Pd/CeO₂ catalysts, and (B) ZnO and various Pd/ZnO catalysts.

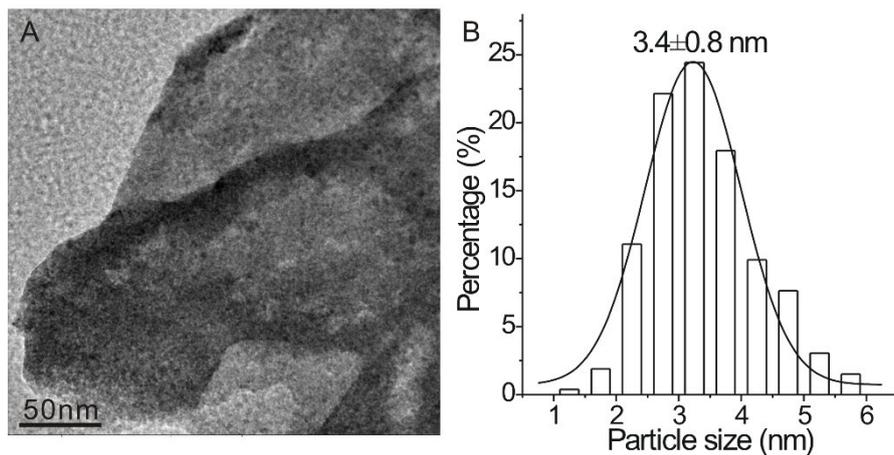


Figure S2. (A) TEM image of typical 2%Pd/CeO₂ catalyst and (B) its corresponding size distribution. According to size distribution, the dispersion of particles was calculated by the equation: Dispersion (%) = $1/d \times 100$, where d refers to the average particle size acquired by TEM. Thus, the calculated dispersion is 29.41%.¹

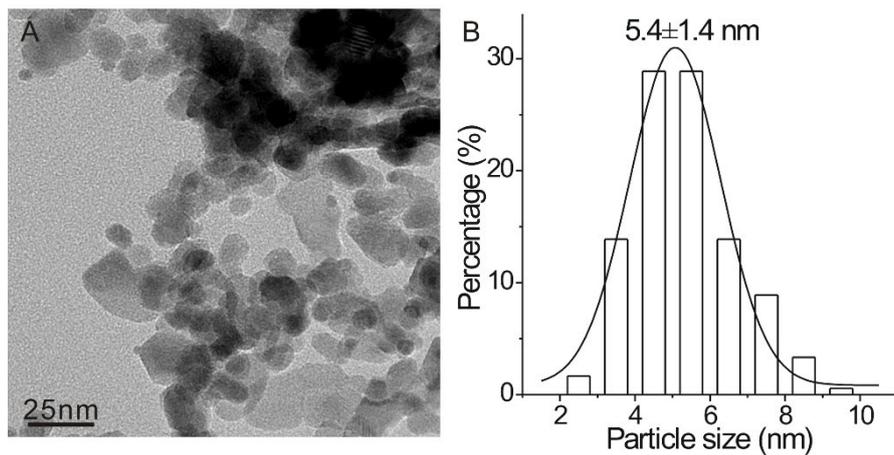


Figure S3. (A) TEM image of typical 2%Pd/ZnO catalyst and (B) its corresponding size distribution. According to size distribution, the dispersion of particles was calculated by the equation: $\text{Dispersion (\%)} = 1/d \times 100$, where d refers to the average particle size acquired by TEM. Thus, the calculated dispersion is 18.52%.¹

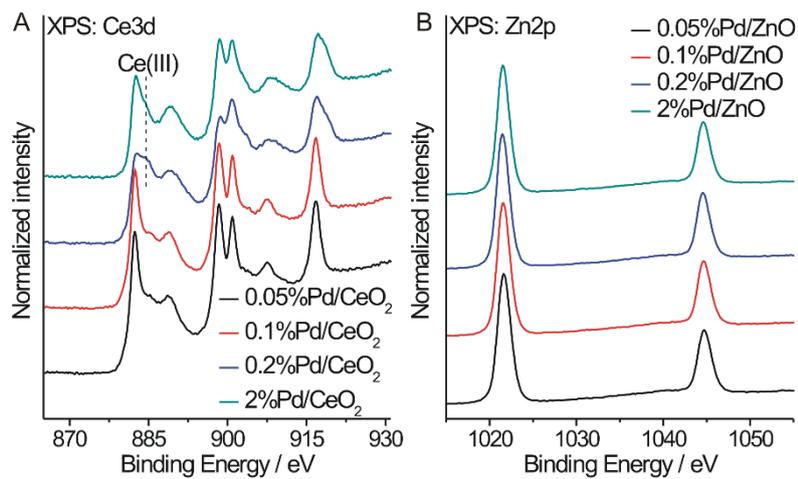


Figure S4. (A) Ce 3d XPS spectra of various Pd/CeO₂ catalysts and (B) Zn 2p XPS spectra of various Pd/ZnO catalysts.

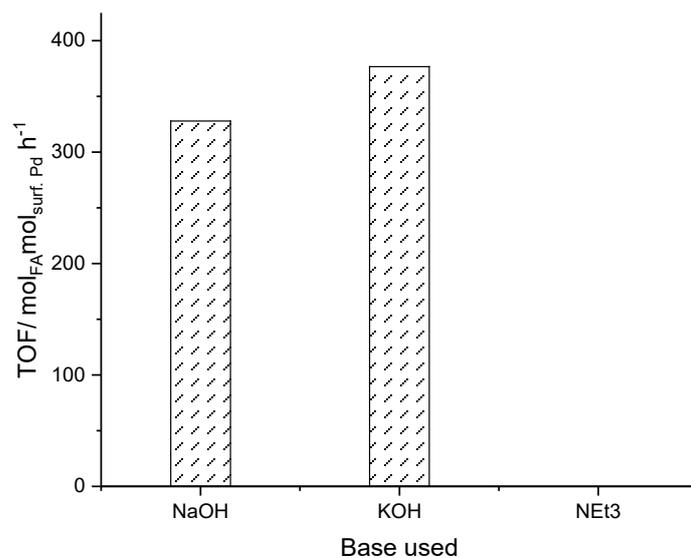


Figure S5. TOFs ($\text{mol}_{\text{FA}} \text{mol}_{\text{surf. Pd}}^{-1} \text{h}^{-1}$) of FA on 2%Pd/TiO₂ catalyst with different aqueous base solutions. Results show that strong inorganic bases like NaOH and KOH are beneficial for the direct hydrogenation of CO₂ whereas NEt₃ as organic amine base does not seem to contribute to the CO₂ hydrogenation reaction.

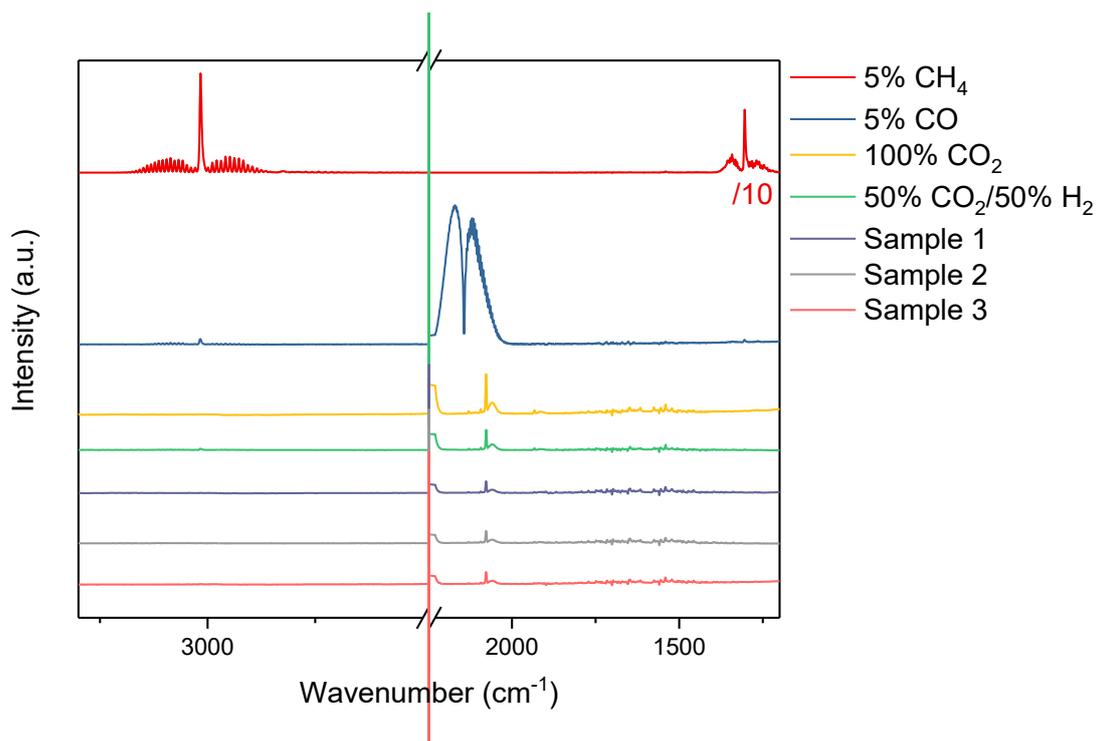


Figure S6. Product selectivities for CO₂ hydrogenation on 2%Pd/TiO₂ catalyst with different aqueous base solutions. Samples refer to the reactions in Fig. S5 (sample 1: NaOH; sample 2: KOH; sample 3: NEt₃). As reference, the reaction mixture (50 vol% CO₂ and 50 vol% H₂), pure CO₂ and dilute CH₄ (5 vol% in Ar) and dilute CO (5 vol% in Ar) were measured by gas phase FTIR as well. No obvious peaks indicating the formation of CO and CH₄ are observable. In the CO₂ FTIR region, the detector is saturated and thus, this region is omitted.

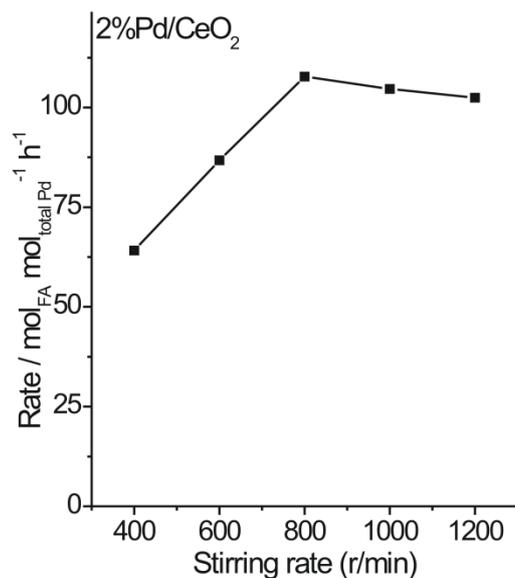


Figure S7. Production rate ($\text{mol}_{\text{FA}} \text{mol}_{\text{total Pd}}^{-1} \text{h}^{-1}$) of FA on 2%Pd/CeO₂ catalyst with different stirring rates. The results show that the optimal stirring rate is 800 r/min, by using this stirring rate, no mass transfer limitation exists on dynamic measurements. Moreover, all FA yield are controlled under 15%, which are far away their equilibrium conversions, indicating that no equilibrium limitation and high conversion limitation exist on our system.

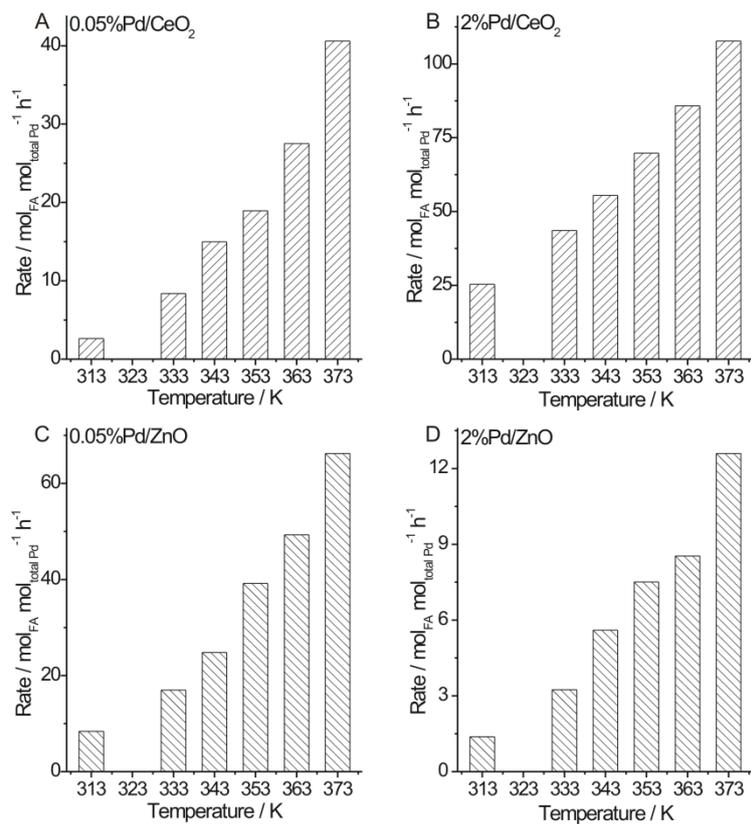


Figure S8. Production rate (mol_{FA} mol_{total Pd}⁻¹ h⁻¹) of FA at different reaction temperature on (A) 0.05%Pd/CeO₂, (B) 2%Pd/CeO₂, (C) 0.05%Pd/ZnO, and (D) 2%Pd/ZnO catalysts.

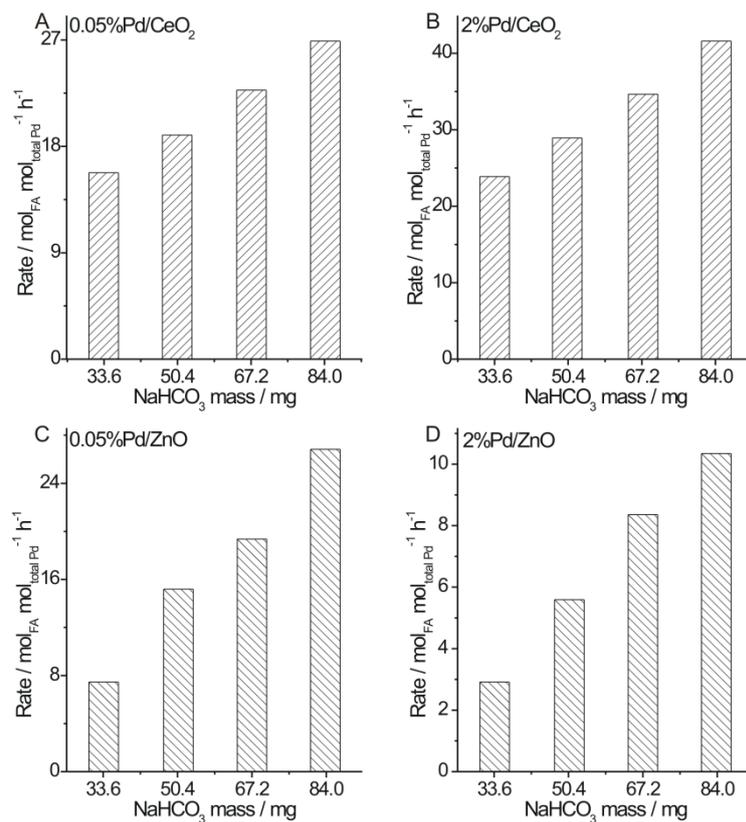


Figure S9. Production rate (mol_{FA} mol_{total Pd}⁻¹ h⁻¹) of FA at the condition of 2 MPa H₂ and various masses of NaHCO₃ (mg) on (A) 0.05%Pd/CeO₂, (B) 2%Pd/CeO₂, (C) 0.05%Pd/ZnO, and (D) 2%Pd/ZnO catalysts.

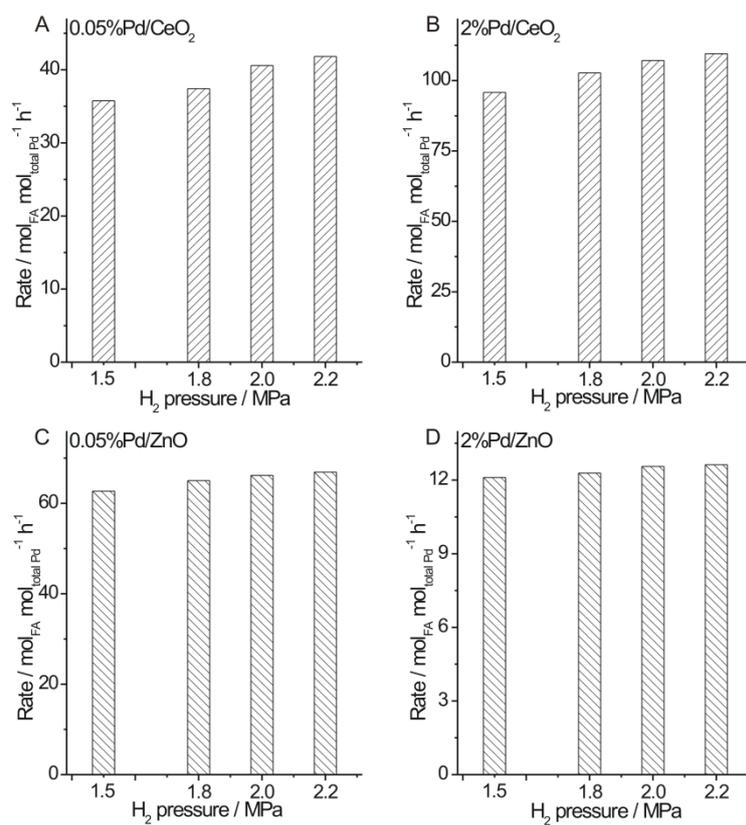


Figure S10. Production rate (mol_{FA} mol_{total Pd}⁻¹ h⁻¹) of FA at the condition of 168 mg NaHCO₃ and various pressures of H₂ (MPa) on (A) 0.05%Pd/CeO₂, (B) 2%Pd/CeO₂, (C) 0.05%Pd/ZnO, and (D) 2%Pd/ZnO catalysts.

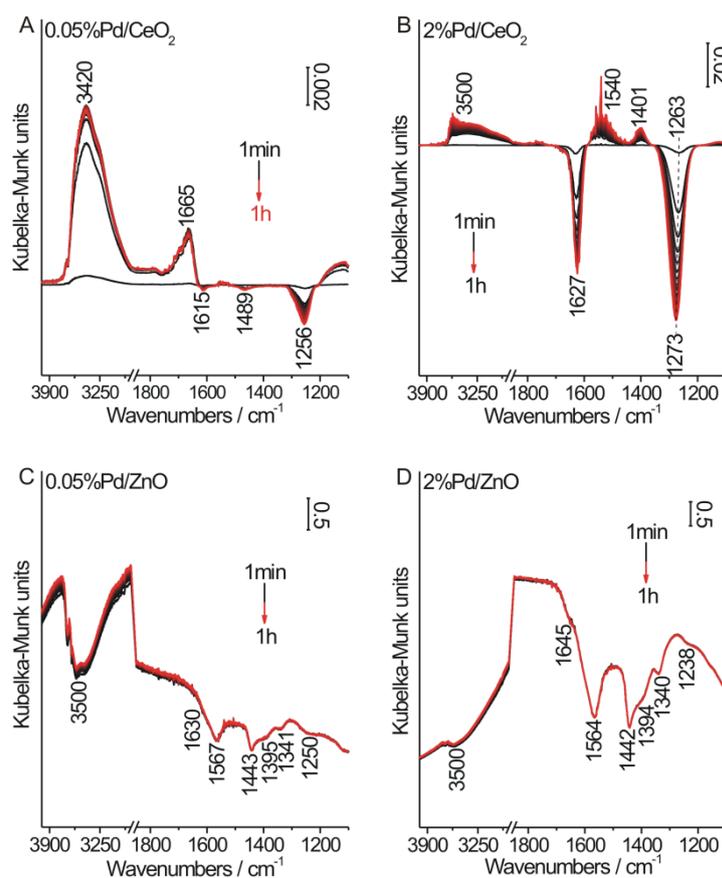


Figure S11. In situ time-resolved DRIFTS spectra of (A) 0.05%Pd/CeO₂ and (B) 2%Pd/CeO₂ catalysts activated by pure H₂ at 373 K for 1 h. On typical Pd/CeO₂ catalysts, a gradual attenuation of bicarbonate and polydentate carbonate accompanying with the enhancement of bidentate carbonate and hydroxyl groups appear on 0.05%Pd/CeO₂ catalyst, and a gradual attenuation of bicarbonate accompanying with the enhancement of monodentate carbonate and hydroxyl groups appear on 2%Pd/CeO₂ catalyst. However, the attenuations of surface bicarbonate, bidentate formate, and unassigned carbonate, and hydroxyl groups are rapid and significant on both 0.05%Pd/ZnO and 2%Pd/ZnO catalysts. It is generally well-known that the activation of H₂ occurs on the surface of Pd.² Thus, these observations indicate that the reaction between atomic H and surface carbonaceous species on Pd/ZnO catalysts is much more rapid compared to Pd/CeO₂ catalysts, in consistency with the higher reaction order of H₂ on Pd/CeO₂ catalysts.

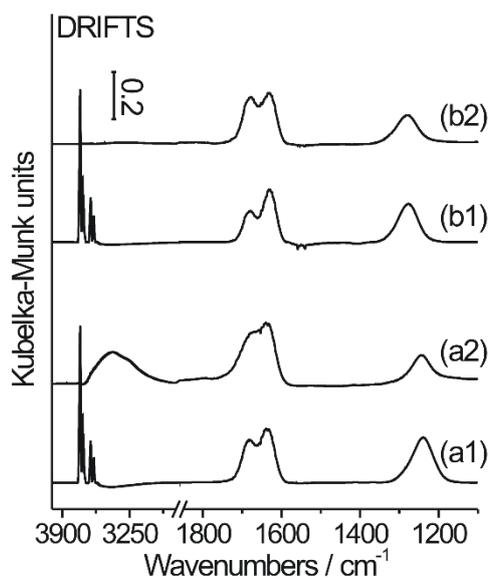


Figure S12. In situ DRIFTS spectra of 0.05%Pd/CeO₂ and 2%Pd/CeO₂ catalysts acquired after activation by pure H₂ at 373 K for 1 h (a1, b1) immersed into CO₂ at 373 K for 1h, and then (a2, b2) purged by high-pure N₂ at 373 K for 30 min, respectively.

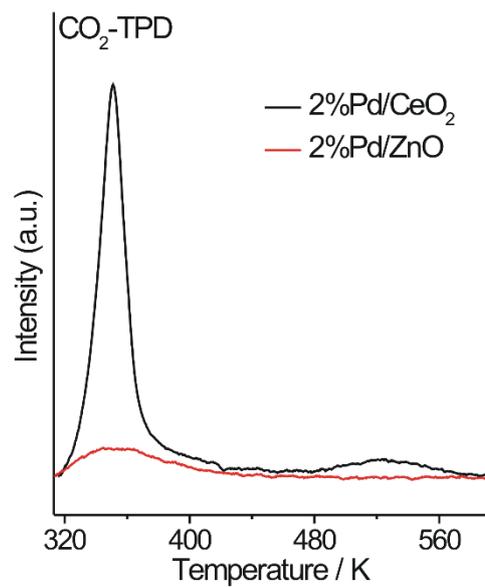


Figure S13. CO₂-TPD profiles of 2%Pd/CeO₂ and 2%Pd/ZnO catalysts.

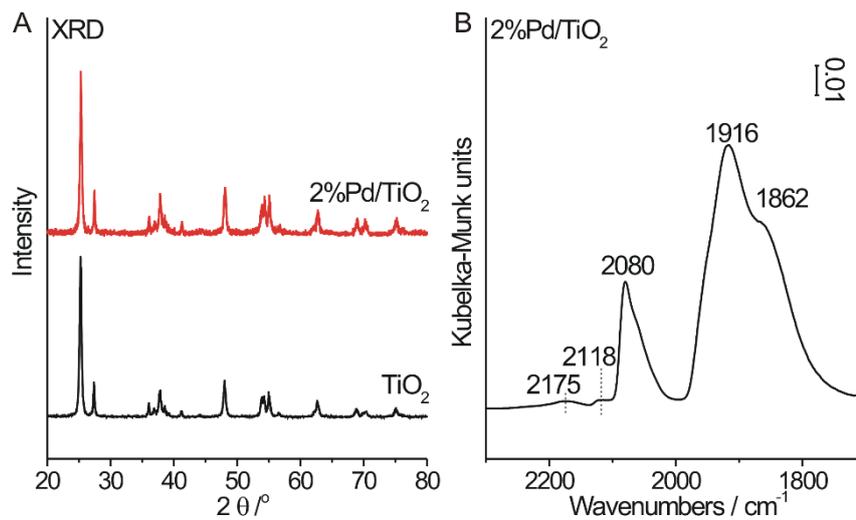


Figure S14. (A) XRD patterns of TiO₂ and 2%Pd/TiO₂ catalysts; (B) in situ DRIFTS of CO adsorption on 2%Pd/TiO₂ at room temperature.

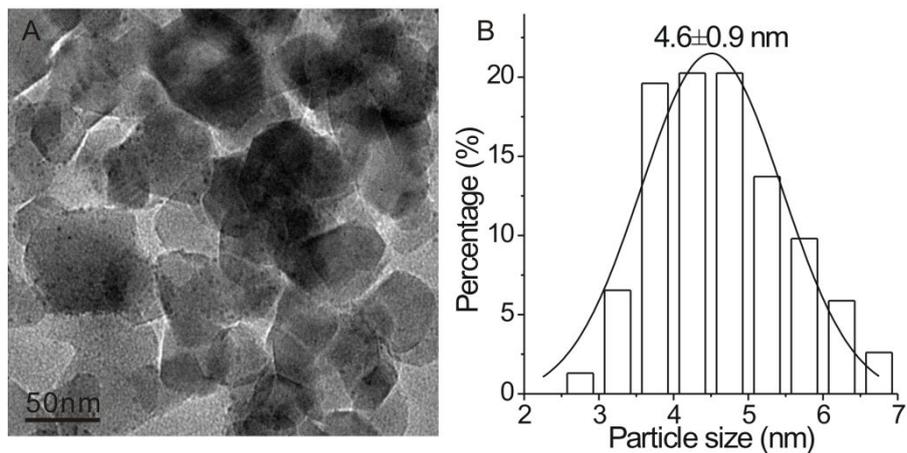


Figure S15. (A) TEM image of 2%Pd/TiO₂ catalyst and (B) its corresponding size distribution. According to size distribution, the dispersion of particles was calculated by the equation: $\text{Dispersion (\%)} = 1/d \times 100$, where d refers to the average particle size acquired by TEM. Thus, the calculated dispersion is 21.74%.¹

References

- (1) Li, W.; Wang, A.; Liu, X.; Zhang, T. Silica-supported Au-Cu alloy nanoparticles as an efficient catalyst for selective oxidation of alcohols. *Appl. Catal. A-Gen.* **2012**, *433-434*, 146-151.
- (2) Mori, K.; Sano, T.; Kobayashi, H.; Yamashita, H. Surface engineering of a supported PdAg catalyst for hydrogenation of CO₂ to formic acid: elucidating the active Pd atoms in alloy nanoparticles. *J. Am. Chem. Soc.* **2018**, *140*, 8902-8909.