

## Supplementary Information

### Acid pretreatment of support promotes Pd/SiO<sub>2</sub> activity for formaldehyde oxidation at room temperature

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**2 Texts; 9 Figures**

## Table of Contents

Text S1. Catalyst preparation

Text S2. Catalyst characterization.

Figure S1. HCHO conversion over Pd/SiO<sub>2</sub>-R, Pd/SiO<sub>2</sub>-0.25M-R, Pd/SiO<sub>2</sub>-0.5M-R, Pd/SiO<sub>2</sub>-1.0M-R and Pd/SiO<sub>2</sub>-2.0M-R catalysts.

Figure S2. HCHO conversion over Pd/SiO<sub>2</sub>-R, Pd/SiO<sub>2</sub>-2h-R, Pd/SiO<sub>2</sub>-4h-R, Pd/SiO<sub>2</sub>-6h-R and Pd/SiO<sub>2</sub>-8h-R catalysts.

Figure S3. (a) HCHO conversion, (b) CO<sub>2</sub> yield over Pd/SiO<sub>2</sub>(HNO<sub>3</sub>), Pd/SiO<sub>2</sub>, SiO<sub>2</sub>(HNO<sub>3</sub>) and SiO<sub>2</sub> catalysts before reduction.

Figure S4. CO<sub>2</sub> yield over Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R, Pd/SiO<sub>2</sub>-R, SiO<sub>2</sub>(HNO<sub>3</sub>)-R and SiO<sub>2</sub>-R catalysts.

Figure S5. Nitrogen adsorption-desorption isotherms of Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R, Pd/SiO<sub>2</sub>-R, SiO<sub>2</sub>(HNO<sub>3</sub>)-R and SiO<sub>2</sub>-R catalysts.

Figure S6. H<sub>2</sub>-TPSR control experiment profiles of Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R and Pd/SiO<sub>2</sub>-R catalysts.

Figure S7. *In-situ* DRIFTS spectra over Pd/SiO<sub>2</sub>-R catalyst.

Figure S8. *In-situ* DRIFTS spectra over SiO<sub>2</sub>-R support.

Figure S9. O<sub>2</sub> effect on the activity of the (a) Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R and (b) Pd/SiO<sub>2</sub>-R catalysts

### **Text S1. Catalyst preparation**

SiO<sub>2</sub> (AR grade, Shanghai Aladdin biochemical technology Co., Ltd, China) samples were treated with nitric acid (HNO<sub>3</sub>, AR grade, Sinopharm Chemical Reagent Beijing Co., Ltd, China) solution. In a typical procedure, SiO<sub>2</sub> was dispersed into the nitric acid solution (0, 0.25, 0.5, 1.0 and 2.0 mol·L<sup>-1</sup>) and constantly stirred in a beaker at 30 °C for different time (2, 4, 6, 8h). The mass ratio of solid to liquid was fixed at 1:20. After acid treatment, the mixed liquid was filtered and washed with deionized water until neutral, then dried at 110 °C overnight in an oven. The pretreated sample was denoted as SiO<sub>2</sub>(HNO<sub>3</sub>). The 0.5 wt.% Pd/SiO<sub>2</sub> and 0.5 wt.% Pd/SiO<sub>2</sub>(HNO<sub>3</sub>) catalysts were prepared by impregnation of SiO<sub>2</sub> and SiO<sub>2</sub>(HNO<sub>3</sub>) with Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (Sigma Aldrich) solution, respectively. After ultrasonication for 30 min and then impregnation under stirring for 4 h, the excess water was removed in a rotary evaporator at 60 °C. Finally, the samples were dried at 110 °C overnight. Before the catalytic activity testing, the samples were reduced at 350 °C with flowing 10 vol.% H<sub>2</sub>/N<sub>2</sub> mixed gas at 100 mL·min<sup>-1</sup> for 1 h. After this treatment the catalysts were denoted as Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R, Pd/SiO<sub>2</sub>-R, SiO<sub>2</sub>(HNO<sub>3</sub>)-R and SiO<sub>2</sub>-R.

### **Text S2. Catalyst characterization.**

Before characterization, the samples were reduced in H<sub>2</sub> at 350 °C for 1 h. X-ray powder diffraction (XRD) patterns of the catalyst samples were collected with a PANalytical X'Pert PRO X-ray diffractometer (Cu K<sub>α</sub> as radiation resource, λ=0.154 nm) at 40 kV and 40 mA. The patterns were measured over the 2θ range from 5° to 90° with a scanning step size of 0.02°. The surface areas and pore characteristics of catalysts

were measured by N<sub>2</sub> adsorption/desorption analysis at -196 °C using a physisorption analyzer (BELSORP-max). Before the N<sub>2</sub> physisorption, the catalysts were degassed at 300 °C for 1 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a JEOL JEM 3200FS TEM with 300 kV acceleration voltage.

Fourier transform infrared (FTIR) spectroscopy was performed on a Thermo Fisher IS10 spectrometer using the KBr pellet method. About 2 mg samples were mixed with 160 mg KBr followed by drying under a heat lamp, then the mixture was pressed into a transparent pellet in a die before the FTIR measurements.

Electron spin resonance (ESR) analysis was carried out on a JEOL JES-FA300 ESR spectrometer system. The ESR spectra were performed at a microwave frequency of 9.85 GHz at 77 K without light irradiation.

CO chemisorption, H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR), H<sub>2</sub> temperature-programmed surface reduction (H<sub>2</sub>-TPSR), and CO temperature-programmed reduction (CO-TPR) cycling experiments were performed in a Micromeritics AutoChem II 2920 apparatus equipped with a thermal conductivity detector (TCD) and mass spectrometer detector (MS).

CO chemisorption was measured by a dynamic pulse method. The catalysts (50 mg) were reduced at 350 °C for 1 h in flowing 10 vol.% H<sub>2</sub>/Ar mixed gas, followed by flushing in Ar gas (30 mL·min<sup>-1</sup>) and cooled down to 30 °C. Then pulses of 5 vol.% CO/He mixed gas (10 mL·min<sup>-1</sup>) were introduced to the catalyst until uptake saturation

was obtained. A CO/Pd stoichiometric ratio of 1 has been assumed for the calculation of Pd dispersion [1, 2].

For H<sub>2</sub>-TPR, the samples (50 mg, 40-60 mesh) were pretreated at 300 °C in flowing Ar gas (30 mL·min<sup>-1</sup>) for 1 h. Then a flow of 10% H<sub>2</sub>/Ar was passed through the sample at a rate of 50 mL·min<sup>-1</sup>. The temperature was increased from -50 to 100 °C at a rate of 10 °C·min<sup>-1</sup>, and the H<sub>2</sub> consumption was monitored by TCD after removal of the produced H<sub>2</sub>O.

For H<sub>2</sub>-TPSR, the samples (50 mg, 40-60 mesh) were first reduced with 10% H<sub>2</sub>/Ar at 350 °C for 1 h, followed by purging with He for 30 min to desorb H<sub>2</sub>. The temperature was then cooled down to 25 °C, and then the gas was switched to O<sub>2</sub> for adsorption for 1 h. After that, He flowed for 30 min to remove weakly adsorbed O<sub>2</sub>. Then a flow of 10% H<sub>2</sub>/Ar was passed through the sample at a rate of 50 mL·min<sup>-1</sup>. The temperature was increased from 0 to 425 °C at a rate of 10 °C·min<sup>-1</sup> and the MS signal of H<sub>2</sub>O (m/z=18 ) was recorded. The H<sub>2</sub>-TPSR control experiments and H<sub>2</sub>-TPSR experiments followed similar experimental procedures, the difference being that after He flowed for 30 min to remove weakly adsorbed O<sub>2</sub>, He was introduced instead of 10% H<sub>2</sub>/Ar.

The CO-TPR cycling experiment was performed according to the following steps. The samples (50 mg, 40-60 mesh) were first reduced with 10% H<sub>2</sub>/Ar at 350 °C for 1 h, followed by purging with He for 30 min to desorb H<sub>2</sub>. The temperature was then cooled down to 30 °C, and then the gas was switched to H<sub>2</sub>O + O<sub>2</sub> for adsorption for 1 h. He flowed for 30 min to remove weakly adsorbed H<sub>2</sub>O + O<sub>2</sub>. Then CO-TPR cycle 1

was performed from 0 to 600 °C (The end temperature was chosen to avoid the influence of hyperthermia on the catalyst). After that, the sample was again pretreated by H<sub>2</sub>O + O<sub>2</sub> for adsorption for 1 h. He flowed for 30 min to remove weakly adsorbed H<sub>2</sub>O + O<sub>2</sub>. Then CO-TPR cycle 2 was performed from 0 to 900 °C.

*In-situ* DRIFTS spectra were recorded with a FTIR spectrometer (Thermo Fisher IS50 FT-IR) equipped with an *in-situ* diffuse reflectance chamber (Harrick) and a liquid N<sub>2</sub> cooled MCT/A detector. Before recording each DRIFTS spectrum, the samples were reduced in flowing 10 vol.% H<sub>2</sub>/N<sub>2</sub> mixed gas at 350 °C for 1 h. All spectra were measured with a resolution of 4 cm<sup>-1</sup> and accumulation of 100 scans. A background spectrum was subtracted from each spectrum.

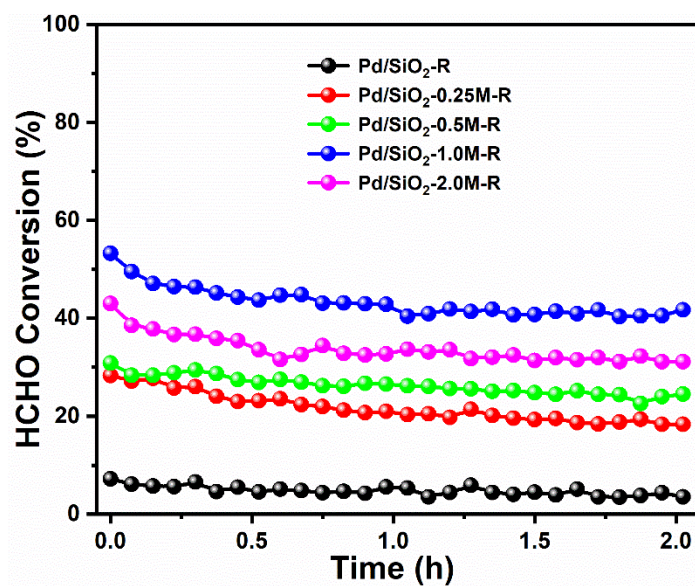


Figure S1. HCHO conversion over Pd/SiO<sub>2</sub>-R, Pd/SiO<sub>2</sub>-0.25M-R, Pd/SiO<sub>2</sub>-0.5M-R, Pd/SiO<sub>2</sub>-1.0M-R and Pd/SiO<sub>2</sub>-2.0M-R catalysts. The catalyst treated with different nitric acid concentration for 6h. Reaction conditions: 150 ppm of HCHO, 20% O<sub>2</sub>, 35% RH, He balance, WHSV 1200,000 mL·g<sup>-1</sup>·h<sup>-1</sup>, at 25 °C.

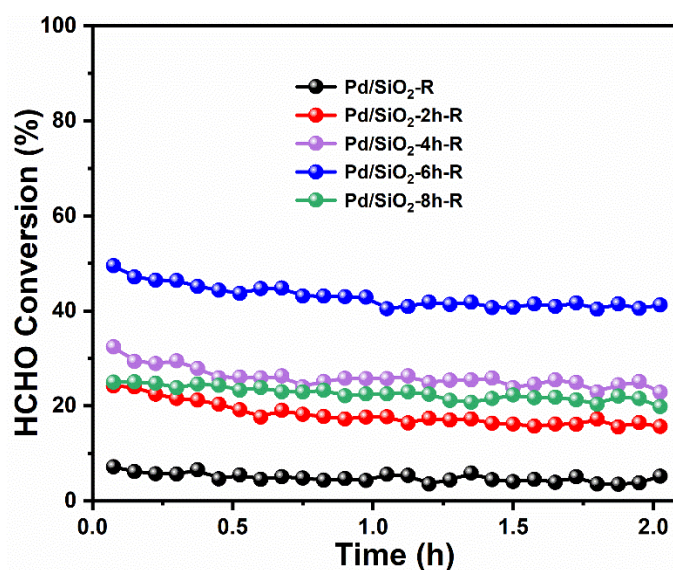
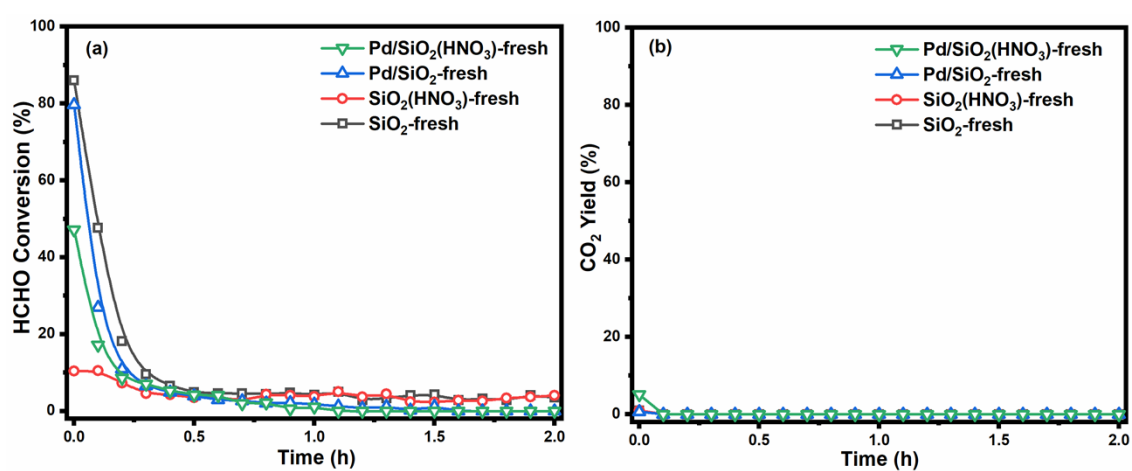
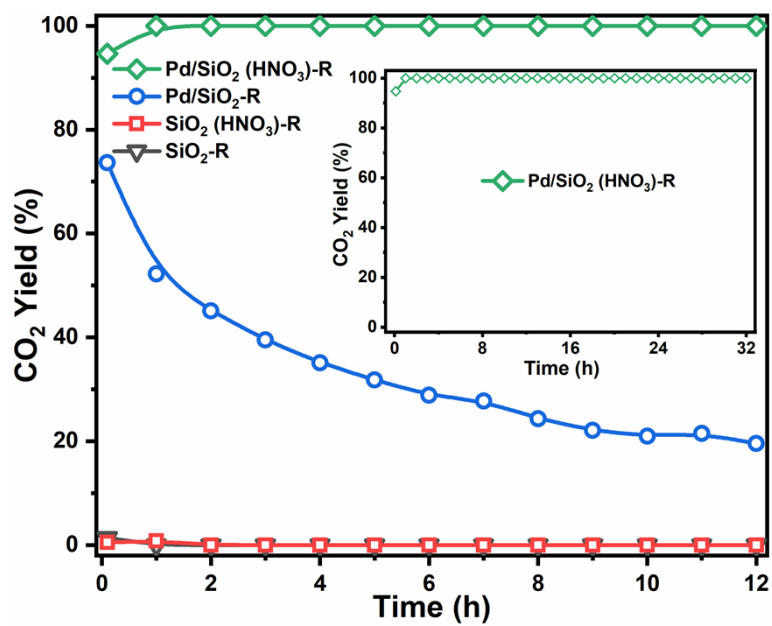


Figure S2. HCHO conversion over Pd/SiO<sub>2</sub>-R, Pd/SiO<sub>2</sub>-2h-R, Pd/SiO<sub>2</sub>-4h-R, Pd/SiO<sub>2</sub>-6h-R and Pd/SiO<sub>2</sub>-8h-R catalysts. The catalyst treated with nitric acid (1.0 mol·L<sup>-1</sup>) for different times. Reaction conditions: 150 ppm of HCHO, 20% O<sub>2</sub>, 35% RH, He balance, WHSV 1200,000 mL·g<sup>-1</sup>·h<sup>-1</sup>, at 25 °C.

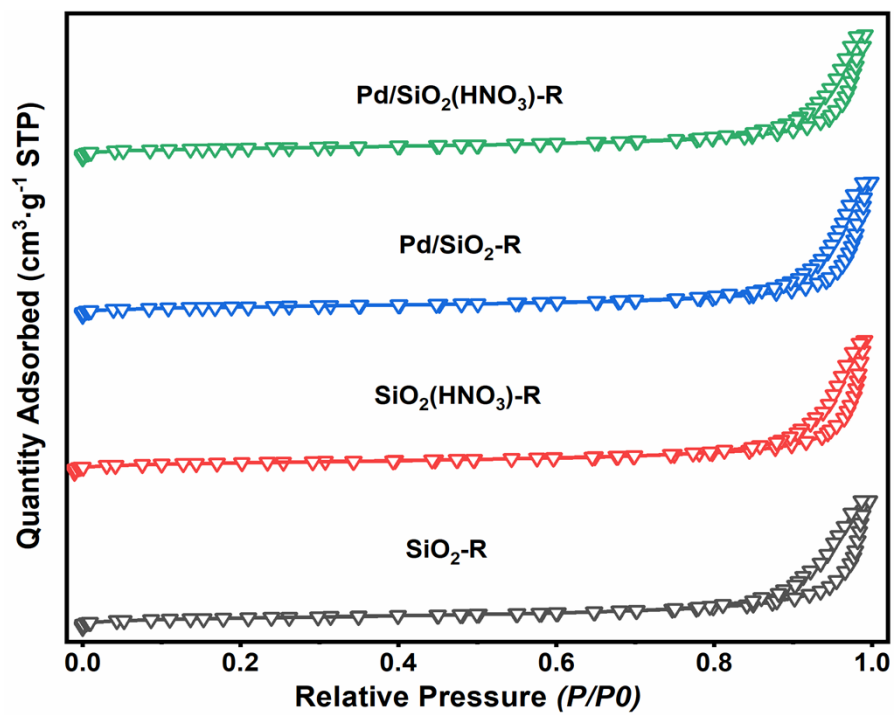


**Figure S3.** (a) HCHO conversion, (b) CO<sub>2</sub> yield over Pd/SiO<sub>2</sub>(HNO<sub>3</sub>), Pd/SiO<sub>2</sub>, SiO<sub>2</sub>(HNO<sub>3</sub>) and SiO<sub>2</sub> catalysts before reduction. Reaction conditions: HCHO 150 ppm, 20 vol.% O<sub>2</sub>, 35% RH, He balance, WHSV 100,000 mL·g<sup>-1</sup>·h<sup>-1</sup>, at 25 °C.

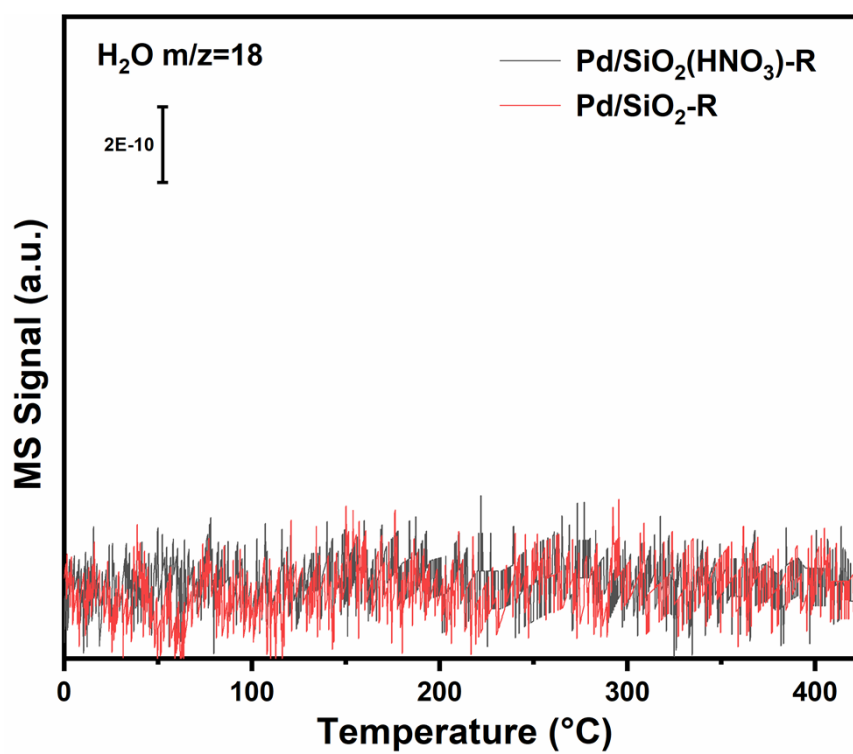




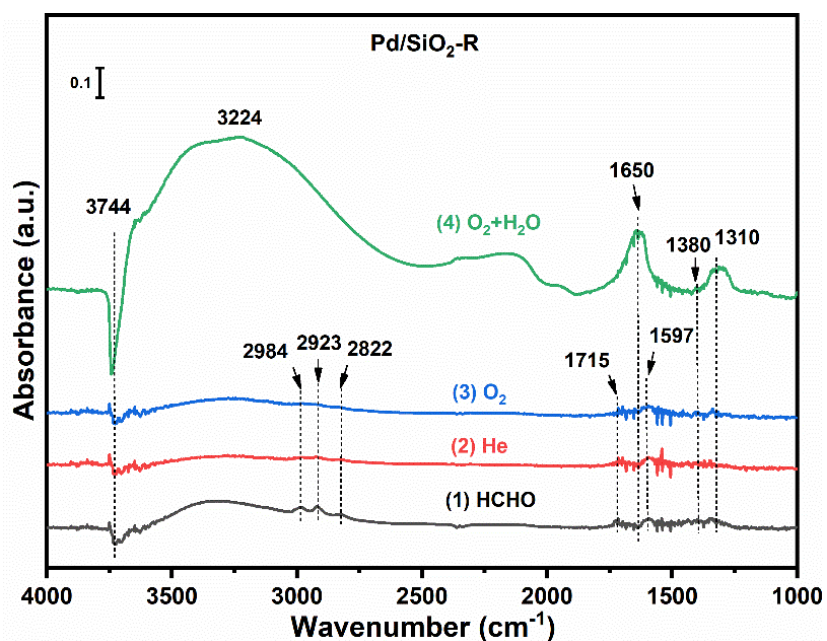
**Figure S4.** CO<sub>2</sub> yield over Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R, Pd/SiO<sub>2</sub>-R, SiO<sub>2</sub>(HNO<sub>3</sub>)-R and SiO<sub>2</sub>-R catalysts. Reaction conditions: HCHO 150 ppm, 20 vol.% O<sub>2</sub>, 35% RH, He balance, WHSV 100,000 mL·g<sup>-1</sup>·h<sup>-1</sup>, at 25 °C.



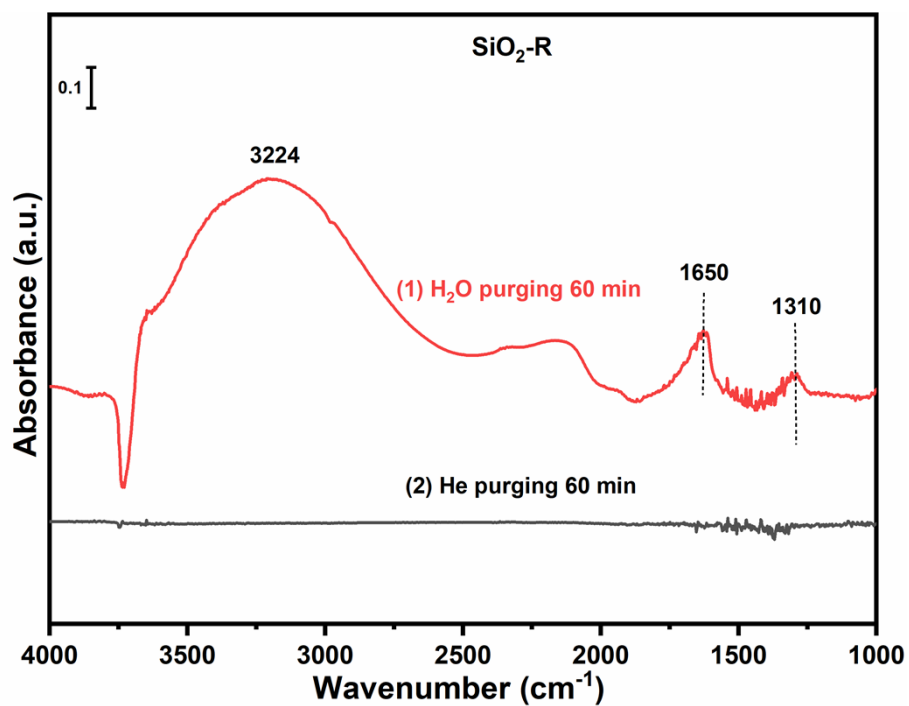
**Figure S5.** Nitrogen adsorption-desorption isotherms of Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R, Pd/SiO<sub>2</sub>-R, SiO<sub>2</sub>(HNO<sub>3</sub>)-R and SiO<sub>2</sub>-R catalysts.



**Figure S6.** H<sub>2</sub>-TPSR control experiment profiles of Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R and Pd/SiO<sub>2</sub>-R catalysts.



**Figure S7.** *In-situ* DRIFTS spectra over Pd/SiO<sub>2</sub>-R in a flow of HCHO for 60 min (1); followed by He purging for 60 min (2); O<sub>2</sub> purging for 60 min (3); and finally by O<sub>2</sub> +H<sub>2</sub>O purging for 60 min (4) at room temperature. Reaction conditions: 150 ppm of HCHO, 20% O<sub>2</sub>, 35% RH, He balance, total flow rate of 100 mL·min<sup>-1</sup>, at room temperature.



**Figure S8.** *In-situ* DRIFTS spectra over SiO<sub>2</sub>-R in a flow of H<sub>2</sub>O for 60 min (1); followed by He purging for 60 min (2), He balance, total flow rate of 100 mL mL<sup>-1</sup>·min<sup>-1</sup>, at room temperature.

To clarify the effect of O<sub>2</sub> on the catalytic performance, O<sub>2</sub> startup-shutdown cycling experiments were performed, and the results are shown in Fig. S7. As shown in Fig. S7, the Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R and Pd/SiO<sub>2</sub>-R catalysts possessed similar phenomena. There was no catalytic activity for HCHO when the flow gases without O<sub>2</sub> (Zone 1 and Zone 3) on two catalysts. After introducing O<sub>2</sub> into the flow gases (Zones 2 and Zones 4), HCHO conversion drastically increased on two catalysts. The result indicated that O<sub>2</sub> play an important role in HCHO oxidation.

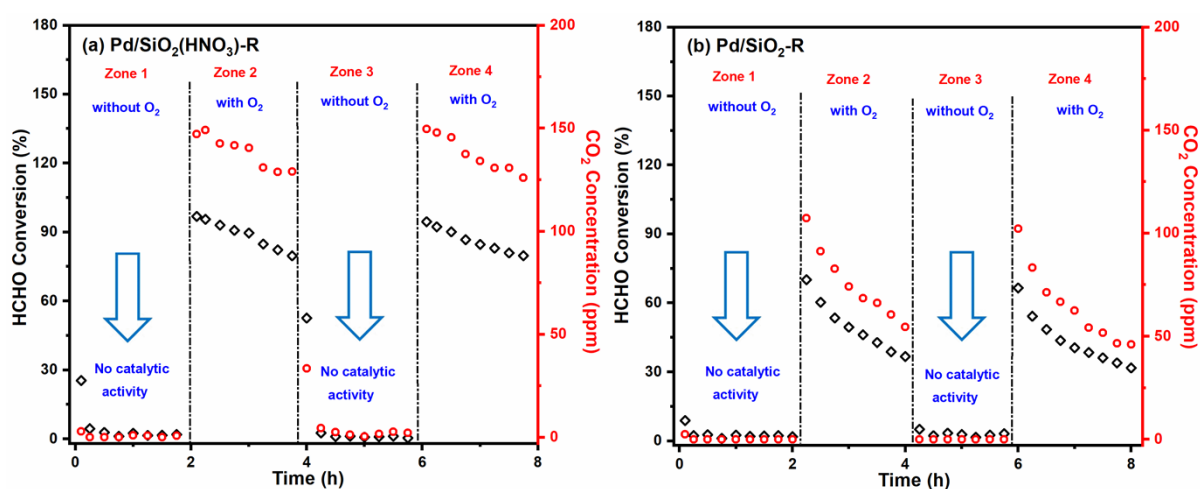


Figure S9. O<sub>2</sub> effect on the activity of the (a) Pd/SiO<sub>2</sub>(HNO<sub>3</sub>)-R and (b) Pd/SiO<sub>2</sub>-R catalysts (Zone 1 and Zone 3, HCHO + He + O<sub>2</sub>; Zone 2 and Zone 4, HCHO + He + O<sub>2</sub> + H<sub>2</sub>O). Reaction conditions: 150 ppm of HCHO, 20% O<sub>2</sub>, 35% RH, He balance, WHSV 300,000 mL·g<sup>-1</sup>·h<sup>-1</sup>, at 25 °C.

## References

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- [2] H. Huang, D.Y.C. Leung, Complete oxidation of formaldehyde at room temperature using TiO<sub>2</sub> supported metallic Pd nanoparticles, *ACS Catal.* 1 (2011) 348-354.