

Electronic Supporting Information

**Enabling Direct Oxidation of Ethane to Acetaldehyde
with Oxygen using Supported PdO Nanoparticles**

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1. Materials and Methods

1.1 Chemical. H-ZSM-5 (Si/Al = 25, Nankai University Catalyst Co., Ltd.), Palladium nitrate ($\text{Pd}(\text{NO}_3)_2$ (Shanghai Titan Scientific Co., Ltd.), deuterium oxide (D_2O , 99.9%, J&K Scientific Co., Ltd.), 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS, 97%, Heowns Co., Ltd.), H_2O_2 solution ($\geq 30\%$) (Shanghai Titan Scientific Co., Ltd.), ethane (C_2H_6 , 99.9%, Air Liquide Co., Ltd.), carbon monoxide (CO , 99.999%, Air Liquide Co., Ltd.), oxygen (O_2 , 99.999%, Air Liquide Co., Ltd.), deionized water from Milli-Q integral water purification system (Millipore, $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$).

1.2 Synthesis of Pd/ZSM-5 series catalysts. Pd/ZSM-5 catalysts with various Pd loading were prepared by the impregnation method. 1 g H-ZSM-5 (Si/Al = 25) powder was soaked in 50 ml of $\text{Pd}(\text{NO}_3)_2$ aqueous solution, the mixture was stirred at room temperature for 3 h and vacuum-rotated at $70 \text{ }^\circ\text{C}$. Then dried at $60 \text{ }^\circ\text{C}$ and calcined at $500 \text{ }^\circ\text{C}$ for 4 h in static air to obtain Pd/ZSM-5. Pd/ZSM-5- H_2 was obtained by reducing 3.0% Pd/ZSM-5 with 10% H_2 at $500 \text{ }^\circ\text{C}$ for 4 h. Pd/ZSM-5-used was collected by centrifuging and drying at $60 \text{ }^\circ\text{C}$ after one round reaction. Then the Pd/ZSM-5-used was re-calcined at $500 \text{ }^\circ\text{C}$, and named as Pd/ZSM-5-used-air.

1.3 Synthesis of Pd_{NPs}/ZSM-5. 1 mL oleylamine (OAm) as protective agents were dissolved in the 30 mL ethylene glycol (EG) to form a turbid solution under vigorous stirring for 1 h. Subsequently, weighted $\text{Pd}(\text{NO}_3)_2$ (mole Pd/OAm = 1/10) dissolved in deionized water was added into the above-mentioned solution and stirred vigorously. Then the mixture solution was heated to $180 \text{ }^\circ\text{C}$ rapidly and refluxed at this temperature for 90 min. After adding 10 mL hexane as an extraction agent to the mixture, it separated into two layers with black-colored hexane on top. The products were precipitated using ethanol and separated by centrifugation. After washing with ethanol several times, the final product was dispersed in hexane to obtain a stable solution of Pd nanoparticles. Pd_{NPs}/ZSM-5 synthesis was synthesized by the same procedure as that of Pd/ZSM-5, except that Pd nanoparticles dispersed in hexane solution were used instead of $\text{Pd}(\text{NO}_3)_2$ aqueous solution.

1.4 Catalytic activity test. The oxidation of the ethane reaction was evaluated in a 35 mL Teflon-coated stainless-steel autoclave. Typically, 20 mg catalysts were added into 10 mL of deionized water. The high-pressure reactor then was filled with 4 bar O_2 , 5 bar CO , and 20 bar ethane after being flushed with the O_2 gas five times to expel the air. The reactor was heated to $150 \text{ }^\circ\text{C}$ by a temperature-controllable heating jacket at approximately 1500 rpm (stir only when the temperature reaches $150 \text{ }^\circ\text{C}$), and a thermocouple was inserted into the solution to detect real-time temperature. After 60 minutes, the reactor was cooled down by ice-water mixtures to avoid the loss of volatile products. The products were collected when the temperature was below $10 \text{ }^\circ\text{C}$, liquid products were collected after the catalysts were filtered. The catalyst stability test was measured after collecting the and re-calcined used catalysts at $500 \text{ }^\circ\text{C}$. The components of products (CH_3OH , HCOOH , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CHO , and CH_3COOH) were identified and quantified by ^1H NMR spectra on a Bruker 600 MHz NMR with solvent suppression technique (typical spectrum as Fig. S1). The chemical shifts and splitting for the protons of different products are shown in Table S2. Typically, 0.70 mL of the

obtained liquid components were mixed with 0.10 mL of D₂O solution with ca. 0.02 wt.% 3-(trimethylsilyl)-1-propane-sulfonic acid sodium salt (DSS) as the internal standard in an NMR tube before analysis. The production amount of H₂O₂ was quantified by UV-vis spectrophotometry with acidified K₂TiO(C₂O₄)₂ solution as the chromogenic agent.^{1, 2} The following equations were used to calculate the yield of products and selectivity of acetaldehyde:

$$\text{Yield of products } (\mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}) = \frac{\text{The amount of products } (\mu\text{mol})}{\text{Catalysts (g)} \times \text{reaction time (h)}} \quad (1)$$

$$\begin{aligned} \text{Yield of products } (\text{mol mol}_{\text{metal}}^{-1} \text{ h}^{-1}) & \quad (2) \\ = \frac{\text{The amount of products (mol)}}{\text{Catalysts (g)} \times \text{metal loading}(\%) \div \text{M(g/mol)} \times \text{reaction time (h)}} \end{aligned}$$

$$\text{Selectivity of acetaldehyde } (\%) = \frac{\text{The amount of acetaldehyde } (\mu\text{mol})}{\text{Total products } (\mu\text{mol})} \times 100 \quad (3)$$

1.5 Catalyst Characterization. X-ray powder diffraction (XRD) patterns were obtained from a Bruker D8 focus diffraction spectrometer using Cu K α radiation (1.54056 Å, 40 kV, and 40 mA), scanning from 10 to 80 ° at a speed of 4 °/min. Inductively coupled plasma optical emission spectrometer (ICP-OES) was used to quantify the actual loading of Cu in the fresh and used catalysts on Agilent 725ES. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi spectrometer. Transmission electron microscopy was operated on a ThermoFisher Talos F200X transmission electron microscope. X-ray absorption (XAS) experiments at the Pd K-edge were carried out at BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF). The spectra were collected in transmission modes. Temperature-programmed surface reaction of ethane (C₂H₆-TPSR) was performed on AutoChem II 2920 apparatus, experiments were carried out in a quartz reactor loaded with 50 mg of catalyst sample, using the online MS (HIDEN ANALYTICAL HPR-20 QIC) as the detector. Typically, the sample was firstly pretreated with O₂ at 500 °C for 30 min, and the reactor was cooled to room temperature. Then pure He gas was introduced to remove physisorbed O₂. Finally, He was replaced with 1 vol.% C₂H₆ flowing at 40 mL min⁻¹. The reactor temperature was raised to 500 °C with the speed at 10 °C min⁻¹ after the stabilization of all the signals. The mass spectrometer was used to track the signal of CO₂, C₂H₆, and H₂ during the reaction. The temperature-programmed desorption of ethanol (CH₃CH₂O-TPD) was performed on the BELCat II apparatus. 100 mg 3.0% Pd/ZSM-5 was pretreated with Ar at 500 °C for 30min, and then pre-adsorbed with ethanol vapor at room temperature for 15 min until saturated. Change to pure Ar to purge excess ethanol vapor for 15 min. The reactor temperature was raised to 250 °C from room temperature with the speed at 10 °C min⁻¹ after the stabilization of the signals, and the ethanol was tracked by mass spectrometry. The temperature-programmed desorption of acetaldehyde (CH₃CHO-TPD) process was almost the same as that of CH₃CH₂OH-TPD, except that acetaldehyde vapor was used for adsorption. The gas-

phase components after the reaction were detected by mass spectrometry (Clarus SQ 8T).

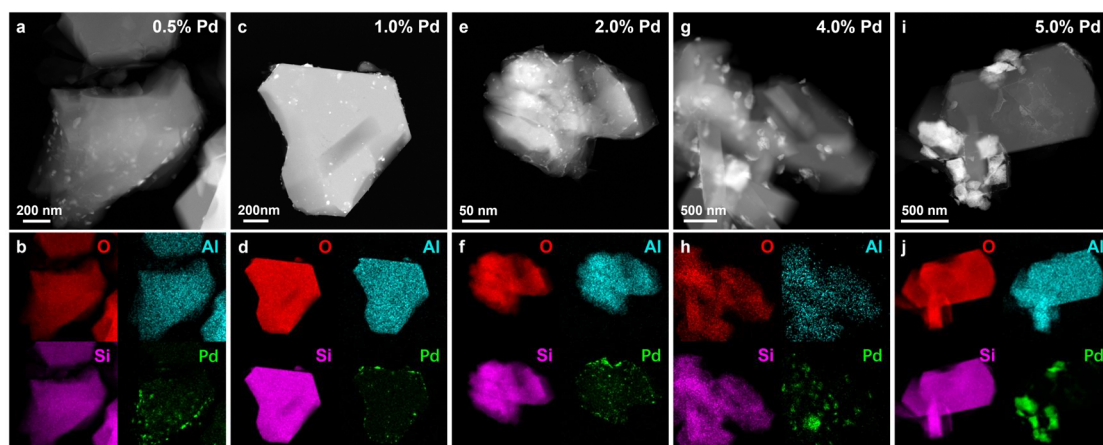


Fig. S1 HAADF-STEM images and the corresponding EDS element maps of (a, b) 0.5% Pd/ZSM-5, (c, d) 1.0% Pd/ZSM-5, (e, f) 2.0% Pd/ZSM-5, (g, h) 4.0% Pd/ZSM-5 and (i, j) 5.0% Pd/ZSM-5.

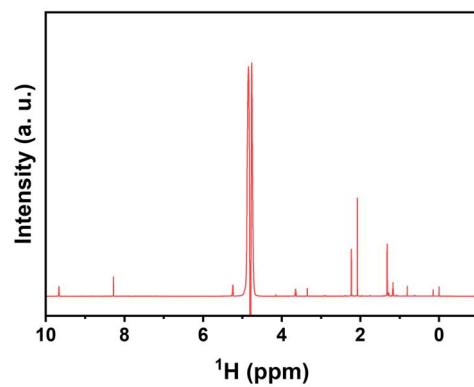


Fig. S2 A typical ^1H NMR spectrum of liquid mixtures after direct oxidation of ethane to acetaldehyde.

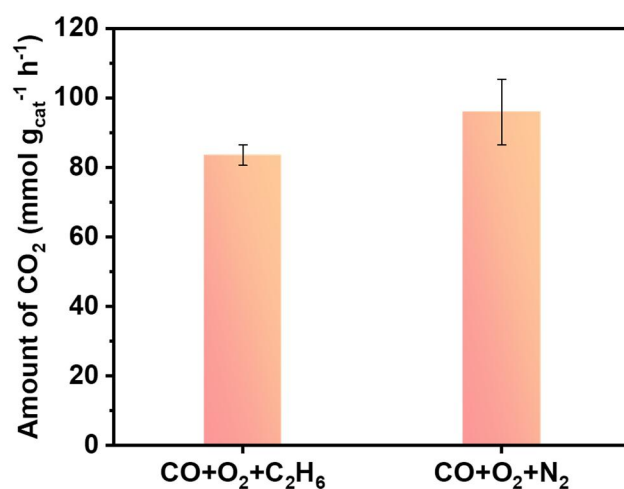


Fig. S3 The production of CO₂ on 3.0%Pd/ZSM-5 catalyst with different gas phase reactants (each reaction tested five times to obtain the average value and error bars). CO+O₂+C₂H₆ condition: 20 mg catalysts, 20 bar C₂H₆, 4 bar O₂, and 5 bar CO, 150 °C, 1h. CO+O₂+N₂ condition: 20 mg catalysts, 20 bar N₂, 4 bar O₂, and 5 bar CO, 150 °C, 1h.

Note: 3.0% Pd/ZSM-5 catalyst was taken as an example to determine the source of CO₂. A yield of 96 mmol g_{cat}⁻¹ h⁻¹ of CO₂ was detected under identical reaction conditions but with N₂ replacing C₂H₆ (CO+O₂+N₂). This allowed us to determine the amount of CO₂ formed from CO. However, under the direct oxidation of ethane conditions (CO+O₂+C₂H₆), a lower amount of CO₂, specifically 85 mmol g_{cat}⁻¹ h⁻¹, was generated on the 3.0% Pd/ZSM-5 catalyst. These results indicate that the direct oxidation of ethane suppresses the CO oxidation reaction on the Pd/ZSM-5 catalyst, suggesting competition between these two reactions. Therefore, accurately determining the production of CO₂ in the direct oxidation of ethane to acetaldehyde is challenging as we cannot calculate the specific amount of CO₂ originating from ethane by simply subtracting the CO₂ produced as a result of CO oxidation from the total amount of CO₂ formed.

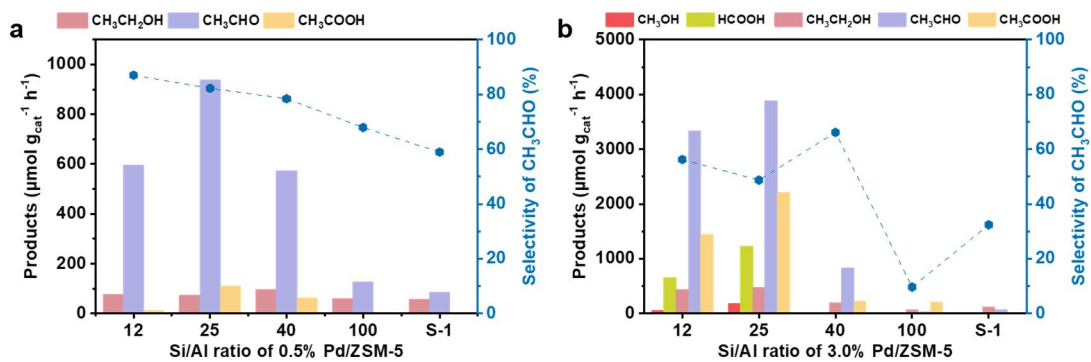


Fig. S4 The effect of Si/Al ratio during the direct oxidation of ethane to acetaldehyde reaction on (a) 0.5% Pd/ZSM-5, (b) 3.0% Pd/ZSM-5. Reaction conditions: 20 mg catalysts, 4 bar O₂, 5 bar CO, 20 bar C₂H₆, 10 mL H₂O, 150 °C, 1 h.

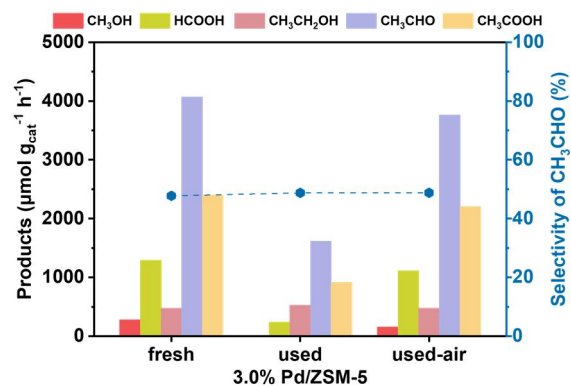


Fig. S5 Product distribution and the selectivity of acetaldehyde of fresh, used, and used-air 3.0% Pd/ZSM-5 catalysts for direct oxidation of ethane to acetaldehyde. Reaction condition: 20 mg catalysts, 4 bar O₂, 5 bar CO, 20 bar C₂H₆, 10 mL H₂O, 150 °C, reaction for 1 h.

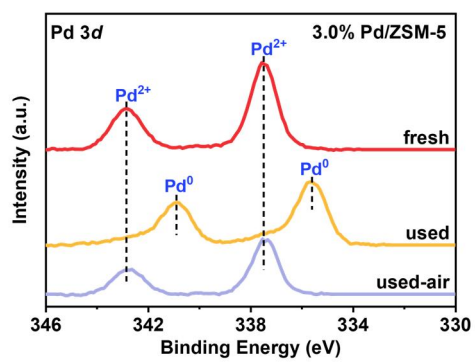


Fig. S6 XPS in Pd 3d region of fresh, used, and used-air of 3.0% Pd/ZSM-5 catalysts.

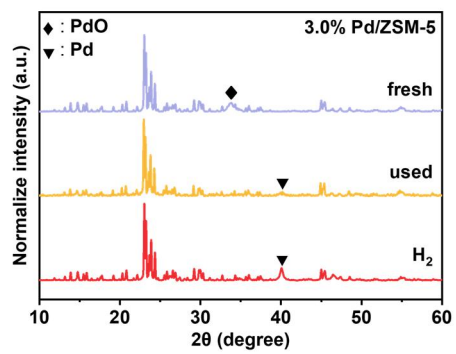


Fig. S7 XRD patterns of different 3.0% Pd/ZSM-5 catalysts.

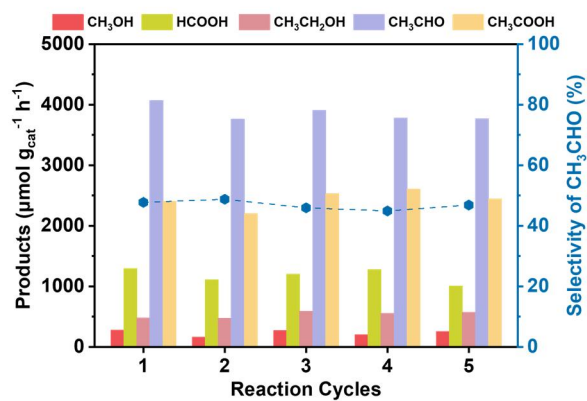


Fig. S8 Stability cycle of Pd/ZSM-5 catalyst in the oxidation of ethane to acetaldehyde. Reaction condition: 20 mg catalysts, 4 bar O₂, 5 bar CO, 20 bar C₂H₆, 10 mL H₂O, 150 °C, reaction for 1 h.

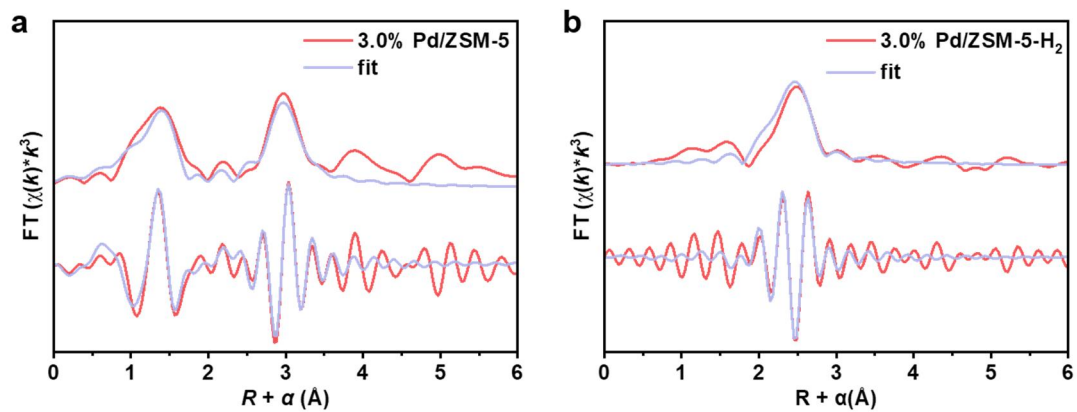


Fig. S9 The fit of the FT EXAFS spectra (top) and the FT imaginary portion (bottom) of a) 3.0% Pd/ZSM-5 and b) 3.0% Pd/ZSM-5-H₂.

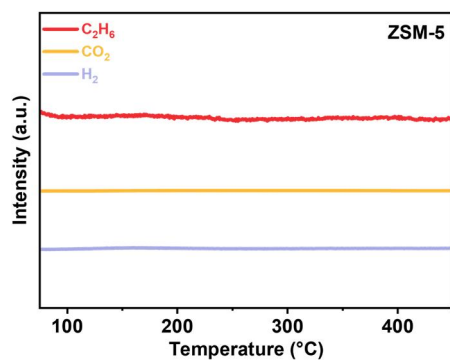


Fig. S10 C₂H₆-TPSR measurement of pure ZSM-5.

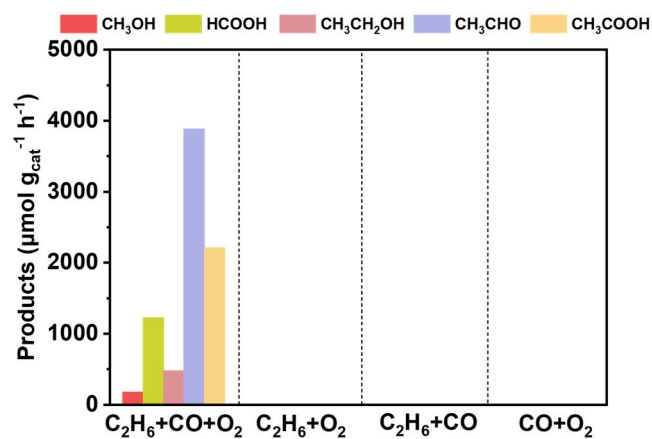


Fig. S11 Catalytic performance with different components of gas reactants on 3.0% Pd/ZSM-5. Reaction condition: 29 bar total gas pressure, containing 4 bar O₂ (if needed), 5 bar CO (if needed), 20 bar C₂H₆ (if needed) and N₂ (balance gas), 10 mL H₂O, 150 °C, 1 h.

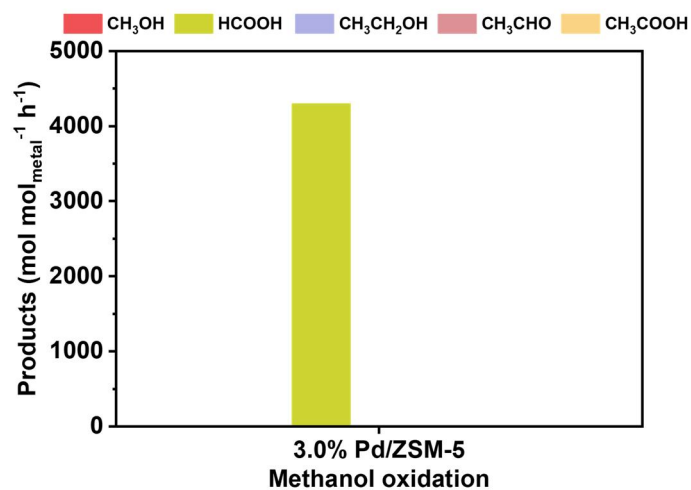


Fig. S12 Product distribution of methanol oxidation on the 3.0% Pd/ZSM-5 catalyst. Reaction condition: 20 mg catalysts, 4 bar O₂, 5 bar CO, 20 bar N₂, 10 mL CH₃OH (0.05 M aq.), 150 °C, 1 h.

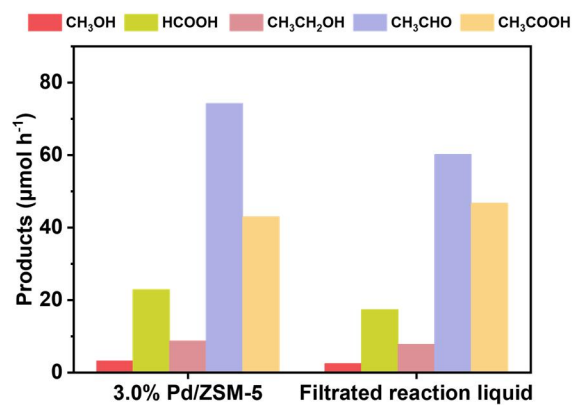


Fig. S13 Catalytic performance on 3.0% Pd/ZSM-5 catalysts and filtrated reaction liquid for direct oxidation of ethane to acetaldehyde. Reaction condition: 4 bar O₂, 5 bar CO, 20 bar N₂, 10 mL H₂O, 150 °C, 1 h.

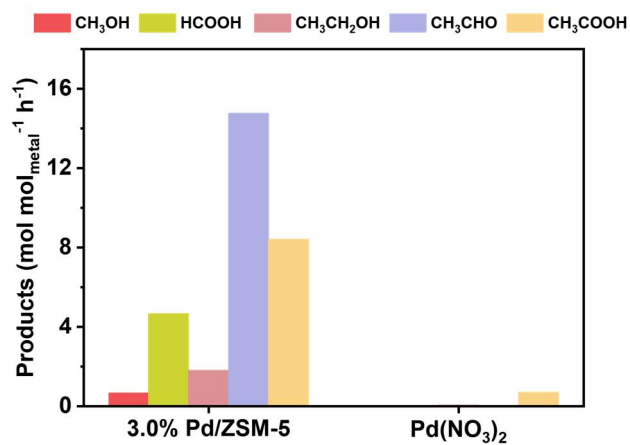


Fig. S14 Catalytic performance on 3.0% Pd/ZSM-5 (20 mg) and 10 mL Pd(NO₃)₂ aqueous solution (Pd: 0.06 g/L) for direct oxidation of ethane to acetaldehyde. Reaction condition: 4 bar O₂, 5 bar CO, 20 bar C₂H₆, 10 mL H₂O, 150 °C, 1 h.

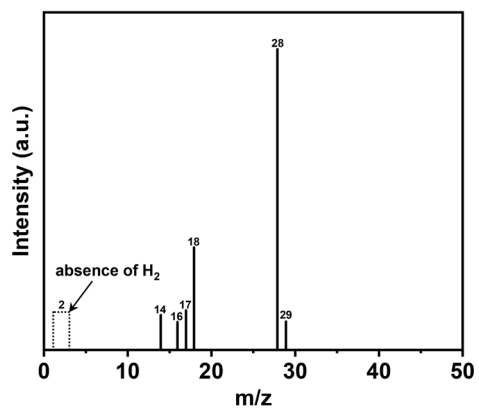


Fig. S15 Gas-phase components after reaction on 3.0% Pd/ZSM-5 detected by mass spectrum. Reaction conditions: 20 mg catalysts, 5 bar CO, 24 bar N₂, 10 mL H₂O, 150 °C, 1 h.

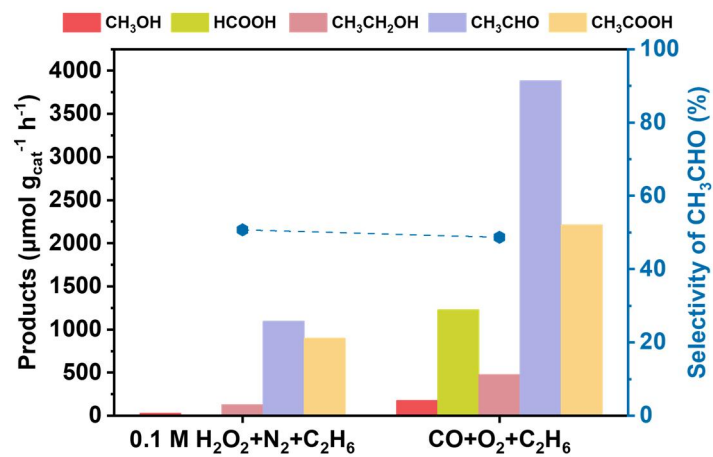


Fig. S16 Comparison of products with H₂O₂ or CO+O₂. H₂O₂ condition: 20 mg catalysts, 10 mL H₂O₂ (0.1M aq.), 9 bar N₂, 20 bar C₂H₆, 150 °C, 1 h. CO+O₂ condition: 20 mg catalysts, 4 bar O₂, 5 bar CO, 20 bar C₂H₆, 10 mL H₂O, 150 °C, 1 h.

Table S1 Chemical compositions of catalysts.

Catalyst	Theoretical Pd content (wt. %)	Actual Pd content (wt. %) ^a
0.5% Pd/ZSM-5	0.5	0.55
1.0% Pd/ZSM-5	1.0	1.3
2.0% Pd/ZSM-5	2.0	2.1
3.0% Pd/ZSM-5	3.0	2.8
4.0% Pd/ZSM-5	4.0	3.9
5.0% Pd/ZSM-5	5.0	4.7
3.0% Pd/ZSM-5-used (5 rounds of reaction)	-	2.2
Pd _{NPs} /ZSM-5	3.0	3.6

a: Determined by ICP-OES

Table S2 ^1H NMR chemical shifts of ethane oxidation products.

Species	Formula	Chemical shift/multiplicity
DDS	-	$\delta=0.0$ ppm, s
Ethane	C_2H_6	$\delta=0.81$ ppm, s
Water	H_2O	$\delta=4.74$ ppm, s
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	$\delta=1.17$ ppm, t
Acetaldehyde (hydrated)	CH_3CHO	$\delta=1.32$ ppm, d
Acetic Acid	CH_3COOH	$\delta=2.08$ ppm, s
Acetaldehyde	CH_3CHO	$\delta=2.23$ ppm, d
Methanol	CH_3OH	$\delta=3.35$ ppm, s
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	$\delta=3.65$ ppm, q
Acetaldehyde (hydrated)	CH_3CHO	$\delta=5.24$ ppm, q
Formic Acid	HCOOH	$\delta=8.28$ ppm, s
Acetaldehyde	CH_3CHO	$\delta=9.66$ ppm, q

Table S3 Curves fitting parameters for Pd K-edge EXAFS of 3.0% Pd/ZSM-5 and 3.0% Pd/ZSM-5-H₂.

Catalyst	Path	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R-factor
3.0% Pd/ZSM-5	Pd-O	5.9±1.5	1.95±0.02	0.006±0.003	-17.5±2.0	0.020
	Pd-(O)-Pd	4.7±1.3	3.39±0.01	0.002±0.002		
3.0% Pd/ZSM-5-H ₂	Pd-Pd	10.7±2.2	2.74±0.01	0.005±0.001	-4.7±1.5	0.014

N is the coordination number; R is interatomic distance; σ^2 is the Debye-Waller factor; ΔE_0 is inner potential correction; R-factor indicates the goodness of the fit; The obtained S_0^2 of Pd foil was 0.75, and S_0^2 was fixed in the subsequent fitting of Pd K-edge for the samples. Data ranges: $3 \leq k \leq 12.4 \text{ \AA}^{-1}$, $1 \leq R \leq 3.5 \text{ \AA}$.

references

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- 2 Y. Yan, C. Chen, S. Zou, J. Liu, L. Xiao and J. Fan, *Front. Chem.*, 2020, **8**, 252.