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Boosting the catalytic performance of Al_2O_3-supported Pd catalysts by introducing CeO_2 promoters

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Experiment details

Materials

Cerium (III) acetate hydrate ($(CH_3CO_2)_3Ce{\cdot}xH_2O$, Aladdin, ≥99.99%), Aluminum oxide (Al_2O_3, Aladdin, 200-300 mesh ≥70%), Palladium nitrate solution ($Pd(NO_3)_2$, 15g/100g, Shanghai Tuosi Chemical Co., Ltd), Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, Aladdin, ≥99.95%), Sodium hydroxide (NaOH, Aladdin). All materials were used without further purification.

Synthesis

Synthesis of AlCePd catalyst. 0.0664 g of $(CH_3CO_2)_3Ce{\cdot}xH_2O$ and 88 μL of $Pd(NO_3)_2$ solution (2 wt%) were dissolved in 100 mL of deionized water and magnetically stirred for 30 minutes, then added 0.72 g of Al_2O_3 support. After that, it was transferred to an oil bath at 80 °C and kept for 6 h. The obtained product was separated by centrifugation three times with deionized water and then kept in a vacuum oven at 70 °C overnight. Then, the dried sample was calcined in a muffle furnace at a heating rate of 5 °C/min for 3 h at 500 °C, and subsequently treated in 5% H_2/Ar at 250 °C for 2 h to obtain the AlCePd catalyst.

Synthesis of AlPd catalyst. The contrast sample AlPd was prepared by impregnation method. 88 μL of $Pd(NO_3)_2$ solution (2 wt%) and 0.72 g of Al_2O_3 were dispersed in 70 mL of deionized water, and then transferred to an oil bath at 80 °C until the solution was completely evaporated.

Synthesis of CePd catalysts. 23 μL of $Pd(NO_3)_2$ solution (2 wt%) and 0.2 g of ceria nanorods were dispersed in 60 mL of deionized water, and then transferred to an oil bath at 80 °C until the solution was completely evaporated.

Synthesis of CeO_2 nanorods. 1.736 g of $Ce(NO_3)_3{\cdot}6H_2O$ and 19.2 g of NaOH were dissolved in 10 ml and 70 ml of deionized water, respectively. After that, the sodium hydroxide solution was added dropwise to the cerium nitrate solution and stirred at room temperature for 30 minutes, then transferred to a 100 ml stainless steel autoclave reactor and kept at 100 °C for 24 h. The products were collected by centrifugation, washed sequentially with deionized water and ethanol, and finally dried at 60°C overnight.

Synthesis of $(AlCePd)_{co}$ catalysts. First, 0.72 g of Al_2O_3 support was dispersed in 70 ml of deionized water, after which 0.0223 g of $Ce(NO_3)_3{\cdot}6H_2O$ and 88 μL of $Pd(NO_3)_2$ solution were added and stirred at room temperature for 30 minutes. Then it was transferred to an oil bath at 80 °C until the solution was completely evaporated.

Characterization. The crystal structures of catalysts were analyzed using Bruker D8 Focus Powder X-ray diffraction with Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA. Inductively coupled plasma optical emission spectrometry (ICP-OES) analyses were performed with a Varian Liberty 200 spectrophotometer to determine the contents of Pd and Ce. Transmission electron microscope (TEM) images were obtained using TECNAI G2 high-resolution transmission electron microscope with an operating voltage of 200 kV. N_2 adsorption-desorption isotherms were measured using an Autosorb-iQ system, and the specific surface areas of the catalysts were calculated according to the Brunauer-Emmett-Teller (BET) method. The Raman measurements were performed on a Renishaw spectrometer at 532 nm on a Renishaw Microscope System RM2000. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al Kα X-ray radiation as the X-ray source for

excitation. Hydrogen temperature-programmed reductions (H_2-TPR) experiments were carried out using a ChemStar TPx Chemisorption Analyzer (USA). 100 mg of the catalyst was first treated in Ar (30 mL min^{-1}) at 250 °C for 2 h, then cooled to room temperature. After that, the flowing gas was switched to 10% H_2/Ar, and then the samples were heated from 50 °C to 800 °C at a ramping rate of 10 °C min^{-1}. CO temperature-programmed desorption (CO-TPD) experiments were performed using a ChemStar TPx Chemisorption Analyzer (USA). 100 mg of the catalyst was first treated in He gas flow (30 ml min^{-1}) at 200 °C for 2 h, and then cooled to room temperature. Next, the flow gas was switched to 10% CO/Ar and kept at room temperature for 1 h. After that, the catalyst was flushed with He gas flow to remove physically adsorbed CO at room temperature. Then, the samples were gradually heated from 25 °C to 700 °C at a ramping rate of 10 °C min^{-1}.

Catalytic activity tests

The CO oxidation reaction was carried out in a fixed bed flow reactor system at atmospheric pressure. 50 mg of catalyst and 50 mg of quartz sand were ground to make a homogeneous mixture and then placed in a quartz tube. The reaction gas (1% CO + 9% O_2 + 90% Ar) was introduced at a flow rate of 33 ml/min and the temperature was raised from room temperature until the CO was completely converted at a ramp rate of 2 °C/min. The products were monitored online using a chromatograph equipped with a thermal conductivity detector (TCD).

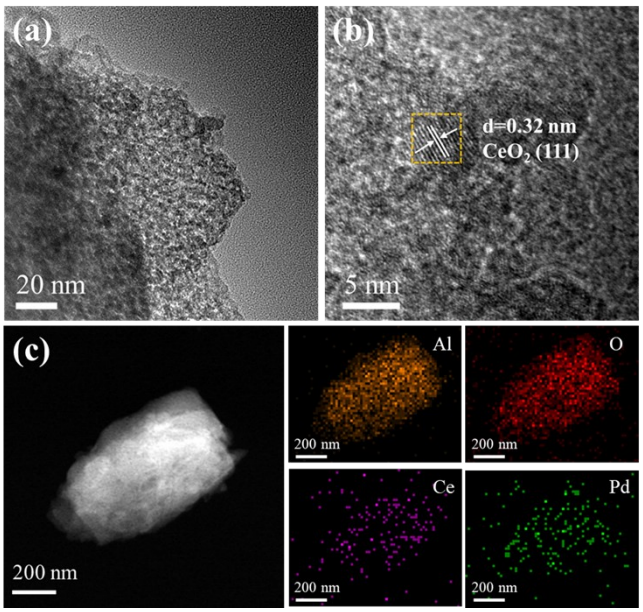

Fig. S1 (a, b) TEM images and (c) EDX elemental mappings of the AlCePd catalyst.

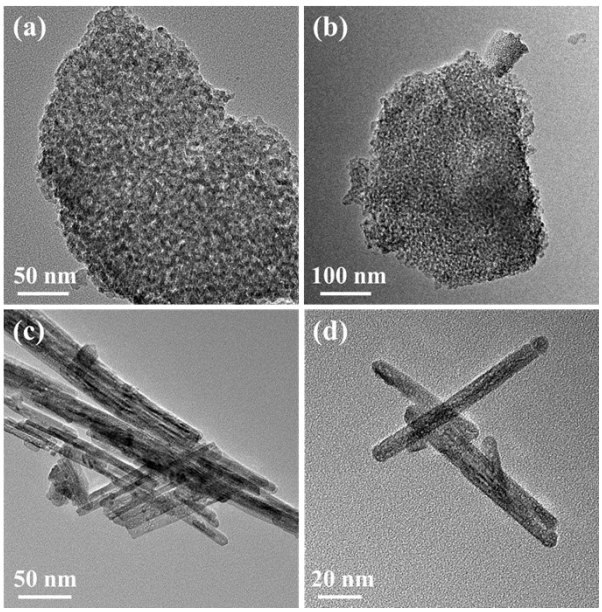

Fig. S2 TEM images of AlPd (a,b) and CePd (c,d).

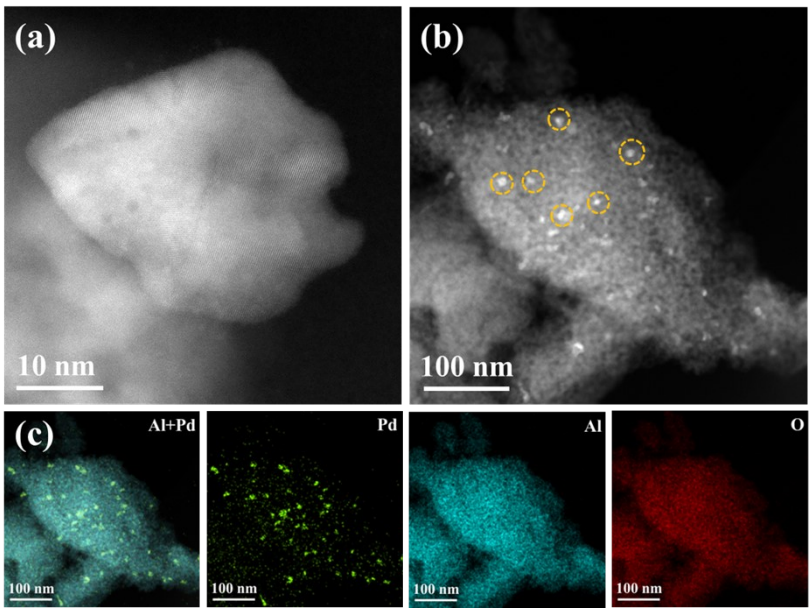

Fig. S3 (a, b) HAADF-STEM images and (c) EDX elemental mappings of the AlPd catalyst. Dotted orange circles in b denote the Pd nanoparticles.

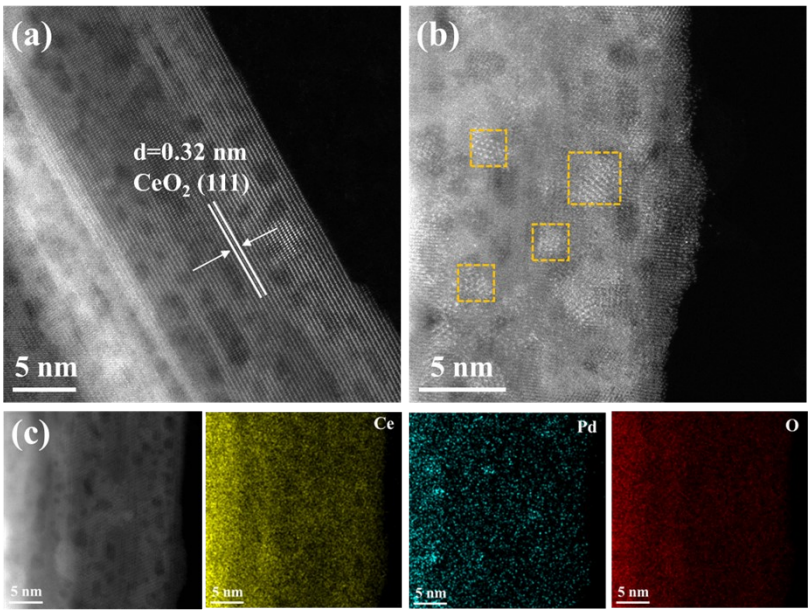

Fig. S4 (a, b) HAADF-STEM images and (c) EDX elemental mappings of the CePd catalyst. Dotted orange boxes in b denote the Pd clusters.

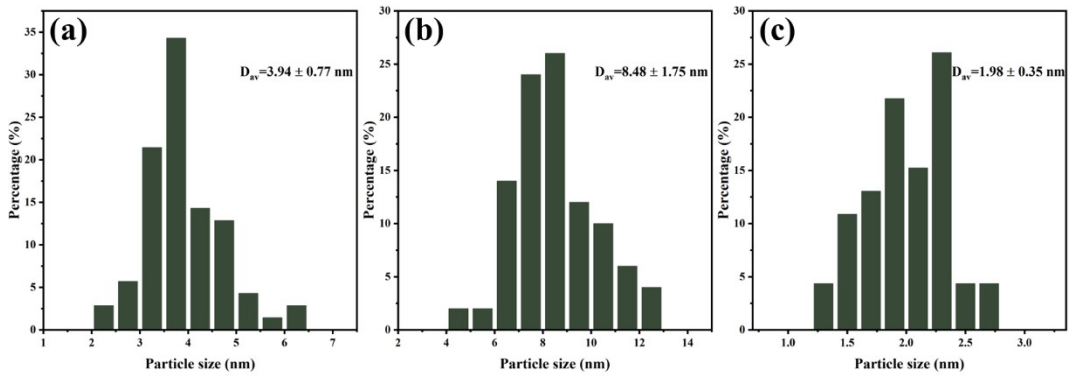

Fig. S5 Average Pd size of AlCePd, AlPd and CePd catalysts.

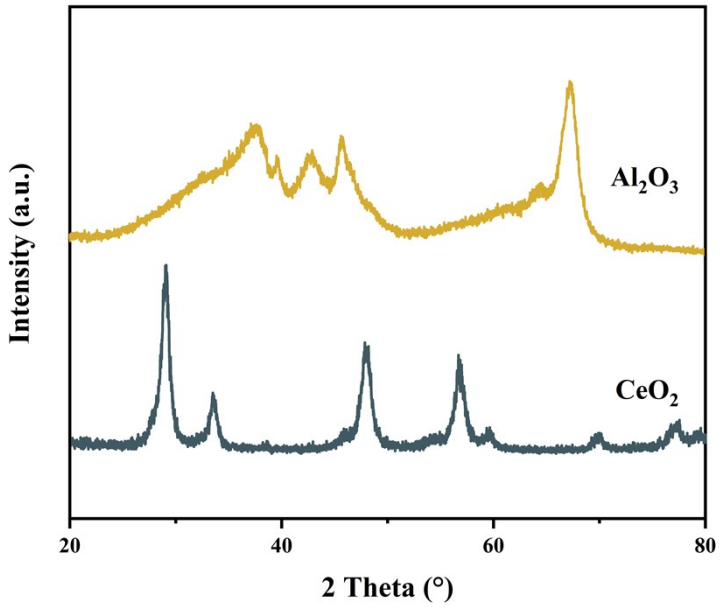

Fig. S6 XRD patterns of Al_2O_3 and CeO_2.

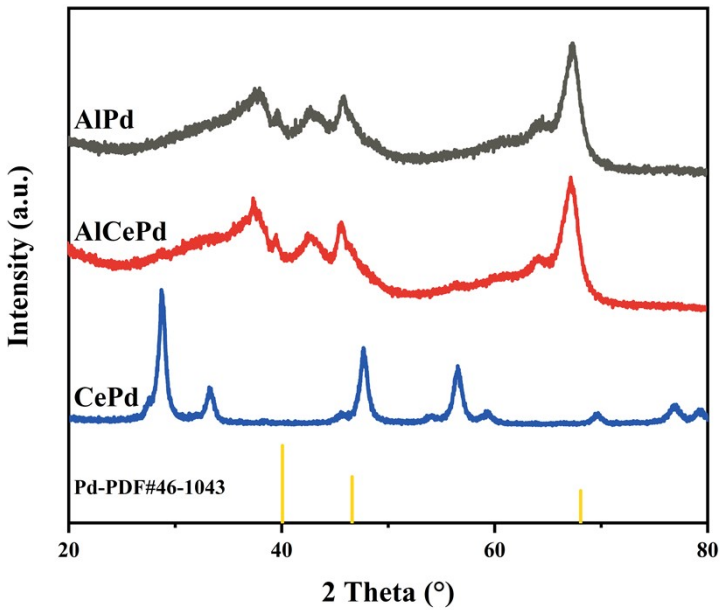

Fig. S7 XRD patterns of fresh AlCePd, AlPd, and CePd catalysts.

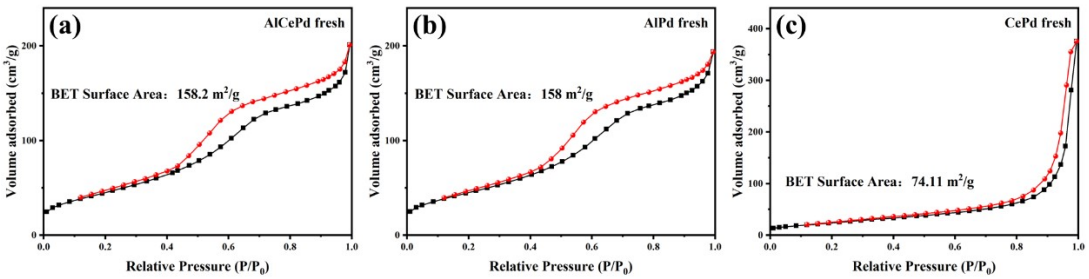

Fig. S8 N_2 adsorption-desorption isotherms of fresh AlCePd, AlPd, and CePd catalysts.

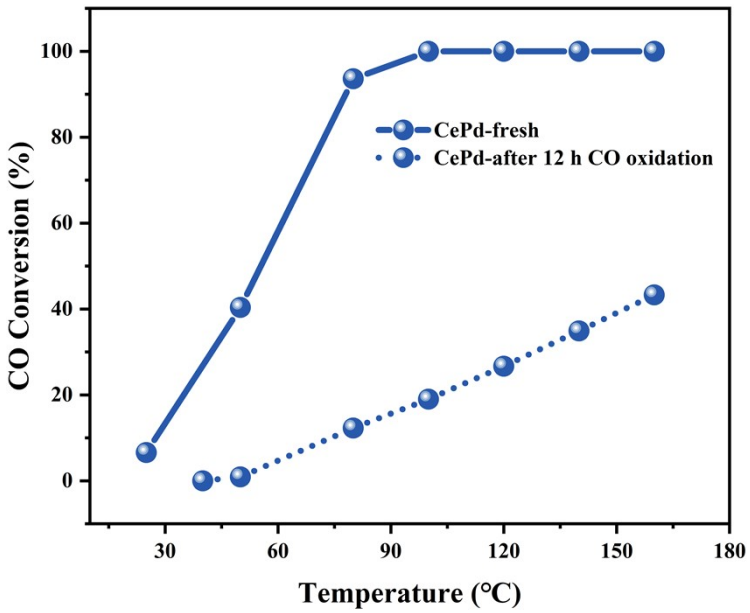

Fig. S9 The profile of CO conversion versus temperature with CePd catalysts before and after long-term CO oxidation tests.

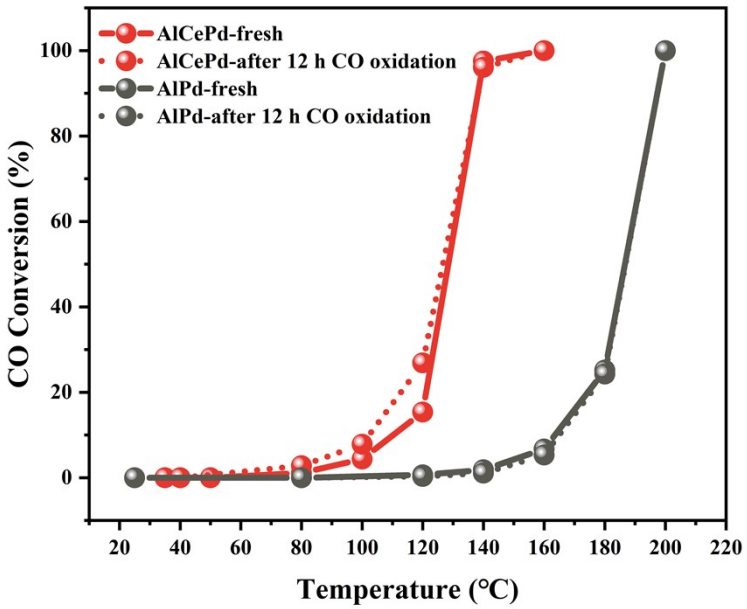

Fig. S10 The profile of CO conversion versus temperature with AlCePd and AlPd catalysts before and after long-term CO oxidation tests.

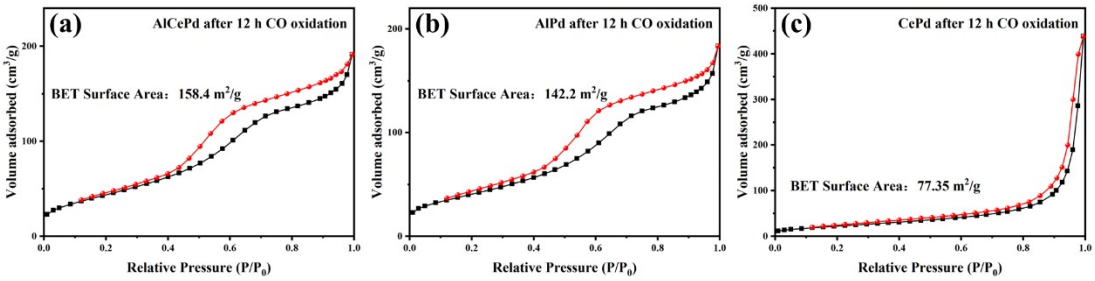

Fig. S11 N_2 adsorption-desorption isotherms of AlCePd, AlPd, and CePd catalysts after long-term CO oxidation tests.

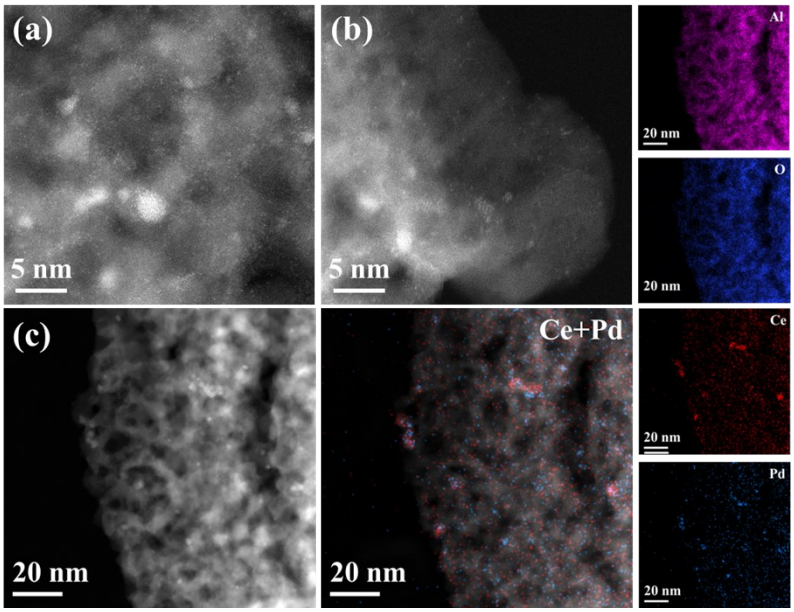

Fig. S12 (a, b) HAADF-STEM images and (c) EDX elemental mappings of the AlCePd catalyst after long-term CO oxidation tests.

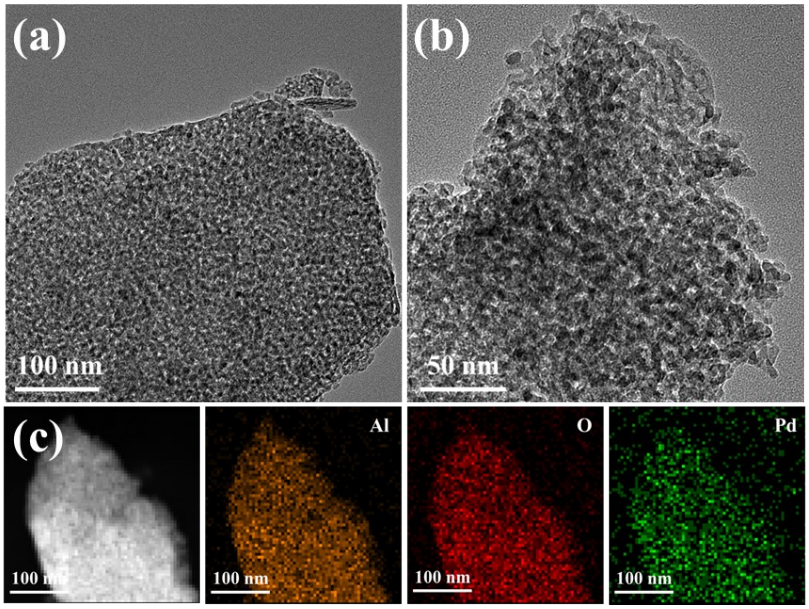

Fig. S13 (a, b) TEM images and (c) EDX elemental mappings of the AlPd catalyst after long-term CO oxidation tests.

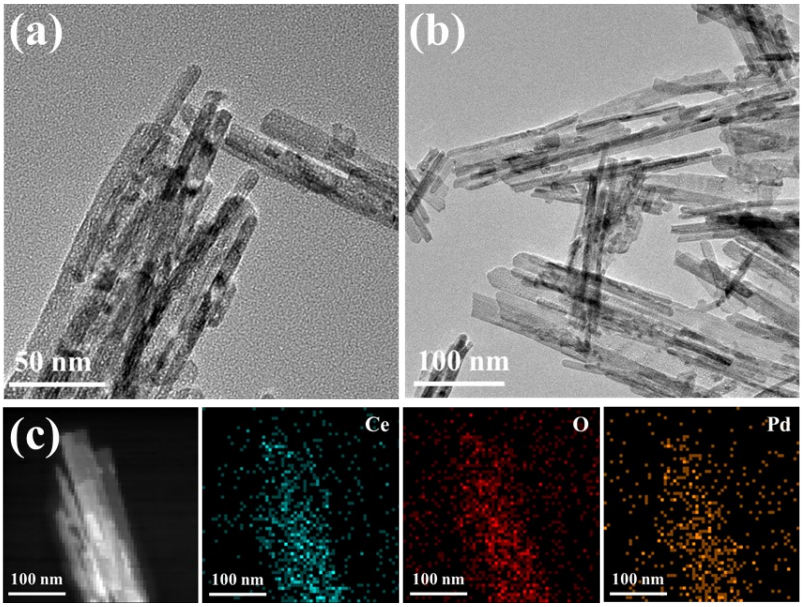

Fig. S14 (a, b) TEM images and (c) EDX elemental mappings of the CePd catalyst after long-term CO oxidation tests.

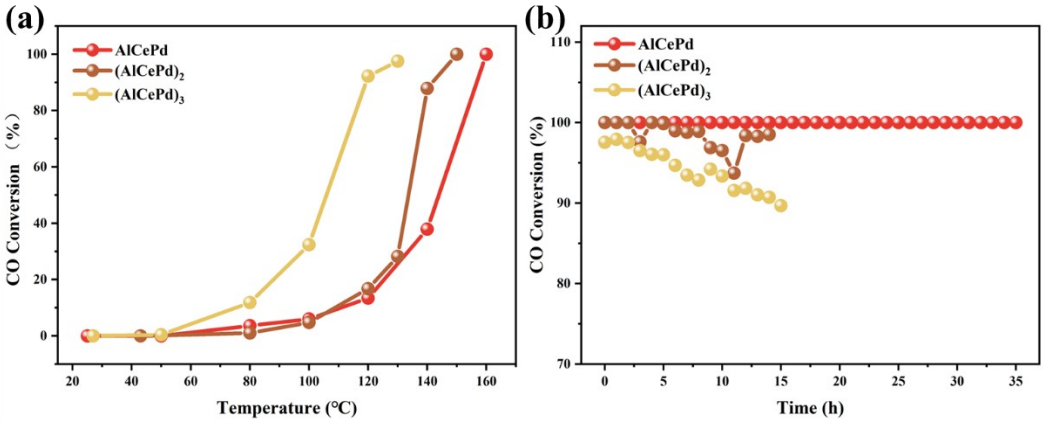

Fig. S15 (a) The profile of CO conversion and (b) the long-term stability with AlCePd catalysts of different Ce contents. The Ce content in AlCePd, $(AlCePd)_2$, and $(AlCePd)_3$ measured by ICP were 0.83%, 1.49%, and 1.72%, respectively.

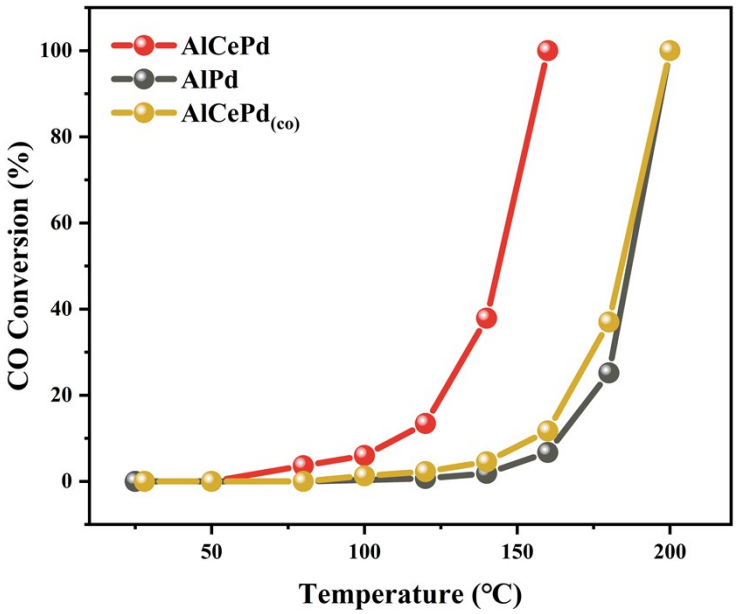

Fig. S16 The profile of CO conversion versus temperature with different catalysts. $AlCePd_{(co)}$ represents the catalyst prepared by co-impregnation.

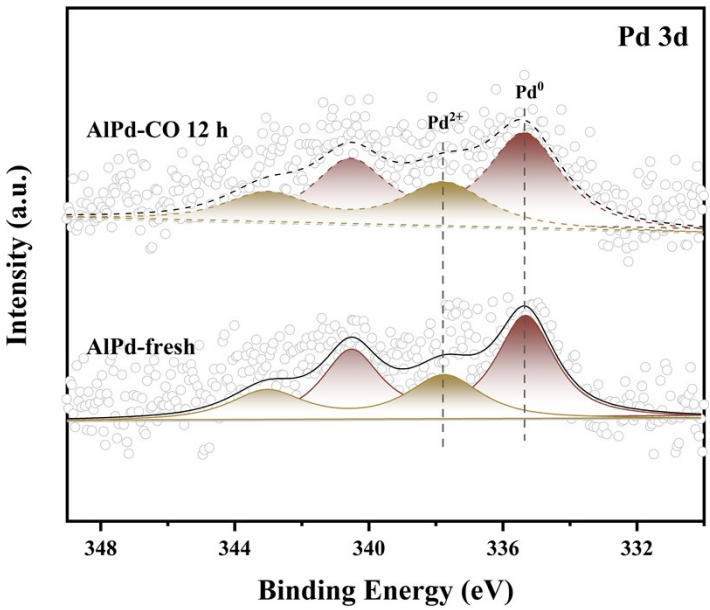

Fig. S17 Pd 3d XPS spectra of AlPd catalysts before and after long-term CO oxidation tests.

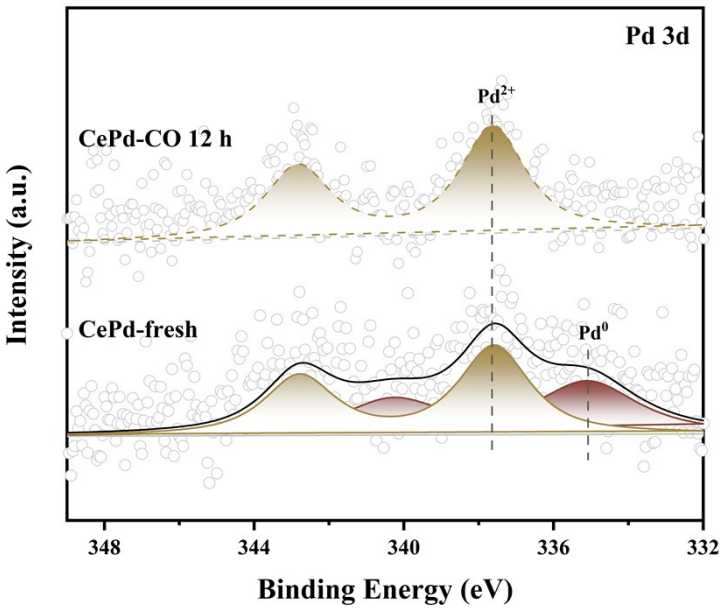

Fig. S18 Pd 3d XPS spectra of CePd catalysts before and after long-term CO oxidation tests.

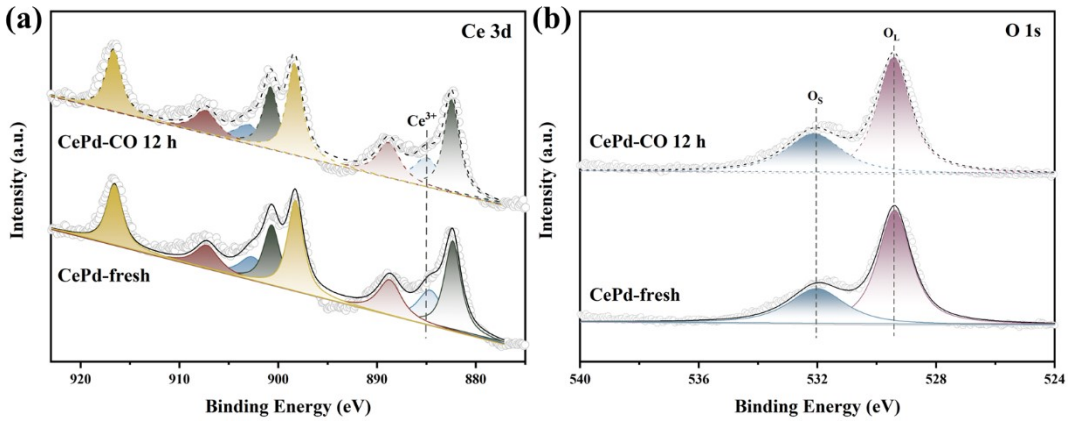

Fig. S19 (a) Ce 3d and (b) O 1s XPS spectra of CePd catalysts before and after long-term CO oxidation tests.

Table S1 Specific surface areas and Pore Diameter of AlCePd, AlPd, and CePd before and after long-term CO oxidation tests.

	AlCePd fresh	AlCePd after 12 h CO oxidation	AlPd fresh	AlPd after 12 h CO oxidation	CePd fresh	CePd after 12 h CO oxidation
S_{BET} (m^2/g)	158.2	158.4	158	142.2	74.11	77.35
Pore Diameter	7.252	7.024	7.051	7.487	24.82	31.15

Table S2 The Pd and Ce contents of AlCePd, AlPd, and CePd catalysts.

	AlCePd	AlPd	CePd
Pd content (wt%)	0.32	0.34	0.32
Ce content (wt%)	0.83	—	—

Table S3 The Pd and Ce contents of $(AlCePd)_2$ 、$(AlCePd)_3$ catalysts.

	$(AlCePd)_2$	$(AlCePd)_3$
Pd content (wt%)	0.36	0.27
Ce content (wt%)	1.49	1.72

Table S4 The T_{50} and T_{90} of different catalysts.

	AlCePd	AlPd	CePd	$(AlCePd)_2$	$(AlCePd)_3$
T_{50} (°C)	143	186	55	133	106
T_{90} (°C)	156	197	78	142	120

Table S5 Percentages of Pd^{2+} and Ce^{3+} content based on XPS analysis of AlCePd, AlPd, and CePd catalysts before and after long-term CO oxidation tests.

	AlCePd fresh	AlCePd after 12 h CO oxidation	AlPd fresh	AlPd after 12 h CO oxidation	CePd fresh	CePd after 12 h CO oxidation
Surface content of Pd^{2+} (%)	40	40.2	35.0	34.9	54.6	100
Surface content of Ce^{3+} (%)	30.9	30.95	—	—	19.4	17.5

Table S6 Comparison of catalysts reported in the literature for CO oxidation.

catalysts	noble metals loading (wt%)	The feed gas (CO : O_2 : balance gas)	WHSV ($ml \cdot g_{cat}^{-1} \cdot h^{-1}$)	T_{100} (°C)	Stability	Reference
AlCePd	0.32	1 : 9 : 90 (Ar)	39600	160	35 h	This work
AlPd	0.34	1 : 9 : 90 (Ar)	39600	200	10 h	This work
CePd	0.32	1 : 9 : 90 (Ar)	39600	120	100%→44% (18 h)	This work
Pd-ZrO_2	0.72	1 : 1 : 98 (He)	180000	>275	16 h	[1]
Pd-CeO_2	0.93	1 : 1 : 98 (He)	180000	>160	2nd cycle	[1]
FeO_x/Pt/CeO_2	0.61	1 : 20 : 79 (Ar)	75000	25	100%→60% (36 h)	[2]
NiO_x/CeO_2	0	1 : 20 : 79 (Ar)	75000	200	—	[2]
Pd/Ce-MOF	5	4 : 20 : 76 (He)	240000	90	8 h	[3]
PdO/CeO_2	1	2 : 8 : 90 (He)	300000	>180	—	[4]
$Ce_{0.984}Pd_{0.016}O_{2-\delta}$	1	2 : 8 : 90 (He)	300000	>280	—	[4]
5Cu/CeO_2	0	1 : 20 : 79 (Ar)	60000	142	T_{100} 143 °C→240 °C (35 h)	[5]
Pd@CeO_2-800 (Ce:CNT=0.12)	1	1 : 1.55 : 97.45 (He)	15000	110	24 h	[6]
Pd/CeO_2-ZrO_2-Al_2O_3	5	1 : 1 : 98 (He)	150000	150	large differences in 11 cycle curves	[7]
Pd/$Ti_{20}Ce_1$	0.5	1 : 10 : 89 (N_2)	72000	200	30 h	[8]

Reference

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