Supporting Information

Engineering multicomponent metal-oxide units for efficient methane combustion over palladium-based catalysts

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Synthesis of supports

Mg-doped $Ce_xZr_{1-x}O_2$-Al_2O_3 supports were synthesized via a modified sol-gel method: 3.06 g of aluminum isopropoxide ($Al(OiP)_3$) was first dispersed in 10 mL of isopropanol and 10 mL of absolute ethanol to form solution A. Then, 1.5 g of triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800) was dissolved in a mixed solution of absolute ethanol (20 mL) and acetic acid (0.18 mL). Afterwards, cerium nitrate (0.1247 g), zirconyl nitrate (0.1020 g) (the theoretical content of cerium and zirconium were both fixed at 5 wt.%) and the required amount of magnesium nitrate were introduced into the above solution to form solution B. Subsequently, the two solutions were mixed slowly and then kept stirring for 4 h. The resulting solution underwent solvent evaporation at room temperature overnight, then dried at 80 ℃ for 10 h. The obtained xerogels were calcined at 500 °C for 4 h (1 °C min^{-1}), then calcined at 900 °C for 1 h (10 °C min^{-1}). Finally, the obtained samples were labelled as 5CZA-yM, where y represented the mass fraction of magnesium (y = 0, 2, 5, 7 wt.%).

As for Al_2O_3 carrier, the synthesis process was similar as above, except that no modified elements were added during preparation process.

Characterization techniques

N_2 physisorption measurements were performed with an ASAP 2460 apparatus. The specific surface area (S_{BET}) was calculated by Brunauer-Emmett-Teller method. The pore volume and pore size distribution originated from the desorption branches of isotherms according to Barrett-Joyner-Halenda model. Powder X-ray diffraction

(XRD) patterns were collected on a Philips X'Pert Pro MPD diffractometer with Cu Kα radiation (1.5406 Å, 45 kV and 40 mA).

Raman spectra were obtained with a Laser Micro-Raman spectrometer, and the used Ar-laser excitation source was λ = 532 nm with a power of 20 mW (spectral resolution of 1 cm^{-1}). UV-visible diffuse (UV-vis) spectra were recorded in the range of 200-800 nm with the scanning rate of 200 nm min^{-1} on a PerkinElmer Lambda 950 spectrophotometer, which used $BaSO_4$ (AR) as the reference substance. X-ray photoelectron spectroscopy (XPS) measurement was conducted on a Thermo ESCALAB 250 spectrometer with monochromatic Al Kα X-ray radiation (hν =1486.6 eV). The binding energies were calibrated against the C 1s at 284.8 eV. Scanning electron microscopy (SEM) images were taken by a Hitachi S-4800 equipment, and the transmission electron microscopy (TEM) images were collected with a FEI Tecnai G2 F20 S-TWIN transmission electron microscope operated at an accelerating voltage of 200 kV.

The in-situ di□use reflectance FTIR spectra of CO adsorption-desorption experiments (CO-DRIFTS) were collected on a Nicolet IS50 FT-IR spectrometer with a high-sensitive MCT. After pretreatment (Ar, 300 °C for 30 min) and pre-reduction (10 vol.% H_2/Ar, 300 °C for 30 min), the CO adsorption DRIFTS experiments were measured under 1 vol.% CO/Ar for 30 min at 30 °C. Finally, the spectra were monitored again after the sample was purged by Ar for 30 min to obtain the desorption spectra.

Temperature-programmed reduction of H_2 (H_2-TPR), temperature-programmed oxidation of O_2 (O_2-TPO) and temperature-programmed desorption of O_2 (O_2-TPD) were implemented on a Micromeritics Autochem II 2920 instrument equipped with a Hiden QIC-20 mass spectrometer and a thermal conductivity detector (TCD). The gas flow rate in each case was set to 30 mL min^{-1}. For H_2-TPR, 150 mg of sample was pretreated in argon at 300 °C for 30 min and then cooled to -50 °C with KWIKCOOL ASSEMBLY. Subsequently, the sample was exposed to 10 vol.% H_2/Ar and then heated to 900 °C (10 °C min^{-1}). In O_2-TPO tests, catalyst (100 mg) was pretreated in He at 350 °C for 30 min, then cooled to 100 °C. Afterward, two rounds of heating/cooling cycles from 100 to 940 °C (10 °C min^{-1}) were continuously conducted under 2 vol.% O_2/He flow. As for O_2-TPD, after pretreatment (He, 350 °C for 30 min), the sample (100 mg) was exposed to 2 vol.% O_2/He (50 mL min^{-1}) to adsorb oxygen for 40 min, then purged in He for 30 min at 50 °C. Afterward, it was heated to 950 °C (10 °C min^{-1}), and the mass signal of O_2 (m/z = 32) was recorded and analyzed.

Temperature-programmed desorption of NH_3 (NH_3-TPD), CO_2 (CO_2-TPD) and CO (CO-TPD) were performed using a Micromeritics Autochem II 2910 instrument equipped with a TCD. The gas flow rate in each case was set to 30 mL min^{-1}. For NH_3-TPD, after pretreatment (He, 300 °C for 30 min), the catalyst (50 mg) underwent pulse adsorption of 8.3 vol. % NH_3/He until saturation at 30 °C. Desorption process was conducted via increasing the temperature to 900 °C (10 °C min^{-1}) under He. CO_2-TPD was similar to that of NH_3-TPD, whereas the adsorbed gas was pure CO_2 (catalyst 200 mg). As for CO-TPD, after pre-reduction (10 vol.% H_2/Ar, 300 °C for 30 min), sample (100 mg) underwent pulse adsorption of 5 vol.% CO/He until saturation at 30 °C. Then, the TPD signals were recorded through heating the catalyst to 900 °C (10 °C min^{-1}) under He flow. The average particle size of Pd and Pd dispersion were calculated with a CO/Pd average stoichiometry of 1.

Table S1. Comparison with literatures about the performance of catalysts for methane oxidation.

catalysts	Methane oxidation performance (℃)	from	Pd (wt.%)	Reaction condition
Pd/5CZA-0M	455 (T_{99})	this work	0.5	1 vol.% CH_4, 5.0 vol.% O_2 in N_2, GHSV = 50,000 mL h^{-1} g^{-1}
Pd/5CZA-2M	420 (T_{99})		0.5	
Pd/5CZA-5M	400 (T_{99})		0.5	
Pd/5CZA-7M	430 (T_{99})		0.5	
Pd/Al_2O_3	485 (T_{99})		0.5	
Pd/ZA-M(A)	500 (T_{100})	1	1.5	750 ppm CH_4, 0.1 vol.% CO, 5.0 vol.% O_2, 12 vol.% CO_2, 12 vol.% H_2O and N_2 balance, GHSV = 50,000 h^{-1}
Pd/ZA(A)	550 (T_{100})	1	1.5	
PdO/CZF/Al_2O_3	280 (T_{100})	2	11.2	1 vol.% methane-air at a rate of 33.4 mL min^{-1}, GHSV = 20,000 L kg^{-1} h^{-1}
PdO/CZB/Al_2O_3	320 (T_{100})	3	11.6	
Pd/Ce-Zr/Al_2O_3	405 (T_{98})	4	2	1.5 vol.% CH_4, 6.0 vol.% O_2 in N_2, GHSV = 18,000 h^{-1}
Pd/Ce-Zr/Al_2O_3	450 (T_{100})	5	0.5	

Table S2. Textural parameters of Pd/Al_2O_3 and Pd/5CZA-yM catalysts.

Sample	S_{BET} [a] (m^2g^{-1})	V_p [b] (cm^3g^{-1})	D_p [b] (nm)
Pd/Al_2O_3	185	0.47	7.6
Pd/5CZA-0M	207	0.28	4.2
Pd/5CZA-2M	178	0.29	7.6
Pd/5CZA-5M	112	0.26	9.9
Pd/5CZA-7M	78	0.26	12.1

[a] calculated by Brunauer-Emmett-Teller (BET) equation.

[b] calculated by Barett-Joyner-Halenda (BJH) method from the desorption branches of N_2 isotherm.

Table S3. CO pulse chemisorption, NH_3-TPD and CO_2-TPD results for Pd/Al_2O_3 and Pd/5CZA-yM catalysts.

Sample	Metal Dispersion[a] (%)	Metal Surface Area[a] (m^2/g_{cat})	Active Particle Size of Pd[a] (nm)	Total acidity (mL/g NH_3 STP)	Total basicity (mL/g CO_2 STP)
Pd/Al_2O_3	32.9	0.73	3.4	1.71	0.21
Pd/5CZA-0M	33.8	0.75	3.3	2.13	0.24
Pd/5CZA-2M	18.7	0.41	5.9	1.66	0.20
Pd/5CZA-5M	16.0	0.36	6.9	1.19	0.19
Pd/5CZA-7M	12.5	0.27	8.9	0.99	0.23

[a] obtained from CO pulse chemisorption (CO/Pd = 1).

Table S4. The detailed information about the oxygen-release peak of PdO in the heating ramp of second TPO cycle over Pd/Al_2O_3 and Pd/5CZA-yM catalysts.

catalyst	α O_2-release peak		β O_2-release peak		γ O_2-release peak	
	Center (°C)	Content (%)	Center (°C)	Content (%)	Center (°C)	Content (%)
Pd/Al_2O_3	732	6.7	794	88.2	853	5.1
Pd/5CZA-0M	759	22.4	811	59.1	875	18.5
Pd/5CZA-2M	741	18.2	791	61.4	840	20.4
Pd/5CZA-5M	718	8.2	786	67.0	843	24.8
Pd/5CZA-7M	752	7.9	809	66.9	851	25.2

Table S5. XPS analyses of O 1s and Ce 3d for catalysts after different treatment.

Catalysts	Relative content / %			O_{ads}/O_{latt}	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$
	O_{OH}	O_{ads}	O_{latt}		
Pd/Al_2O_3-fresh	14.5	71.6	13.9	5.1	-
Pd/5CZA-0M-fresh	10.7	76.8	12.5	6.1	0.46
Pd/5CZA-2M-fresh	14.9	75.4	9.7	7.8	0.52
Pd/5CZA-5M-fresh	12.7	80.8	6.5	12.4	0.61
Pd/5CZA-7M-fresh	12.8	79.0	8.2	9.6	0.57
Pd/Al_2O_3-used	15.0	76.1	8.9	8.6	-
Pd/5CZA-0M-used	15.9	76.7	7.4	10.4	-
Pd/5CZA-2M-used	16.2	77.6	6.2	12.5	-
Pd/5CZA-5M-used	11.5	84.0	4.5	18.7	-
Pd/5CZA-7M-used	20.4	74.4	5.2	14.3	-
Pd/5CZA-0M-stability	15.4	81.6	3.0	27.2	-
Pd/5CZA-5M-stability	13.3	84.2	2.5	33.6	-

Table S6. XPS analyses of Pd $3d_{5/2}$ for catalysts after different treatment.

Catalysts	Pd^0		Pd^{2+}		Pd^{4+}	
	BE (eV)	Content (%)	BE (eV)	Content (%)	BE (eV)	Content (%)
Pd/Al_2O_3-fresh	335.95	26.9	336.89	61.0	337.89	12.1
Pd/5CZA-0M-fresh	335.98	13.2	336.90	56.5	337.88	30.3
Pd/5CZA-2M-fresh	335.94	8.3	336.89	62.5	337.85	29.2
Pd/5CZA-5M-fresh	335.95	6.5	336.85	66.0	337.84	27.5
Pd/5CZA-7M-fresh	335.98	7.2	336.89	64.5	337.89	28.3
Pd/Al_2O_3-used	335.97	29.8	336.87	64.4	338.11	5.8
Pd/5CZA-0M-used	335.98	15.8	336.94	59.3	338.11	24.9
Pd/5CZA-2M-used	335.89	5.4	336.95	73.2	338.14	21.4
Pd/5CZA-5M-used	335.98	4.4	336.94	75.4	338.14	20.2
Pd/5CZA-7M-used	335.96	6.4	337.0	70.7	338.12	22.9
Pd/5CZA-0M-stability	335.99	15.7	336.93	61.5	338.12	22.8
Pd/5CZA-5M-stability	335.98	3.0	336.85	74.8	338.15	22.2

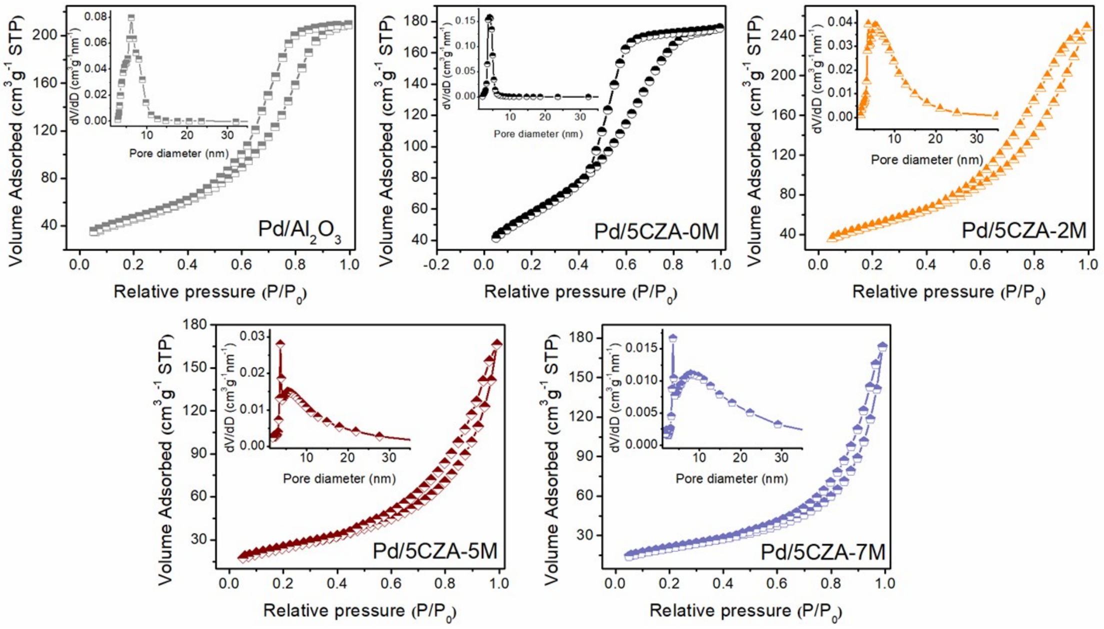

Fig. S1. Nitrogen adsorption-desorption isotherms and corresponding pore size distribution curves (inset) of Pd/Al$_2$O$_3$ and Pd/5CZA-yM catalysts.

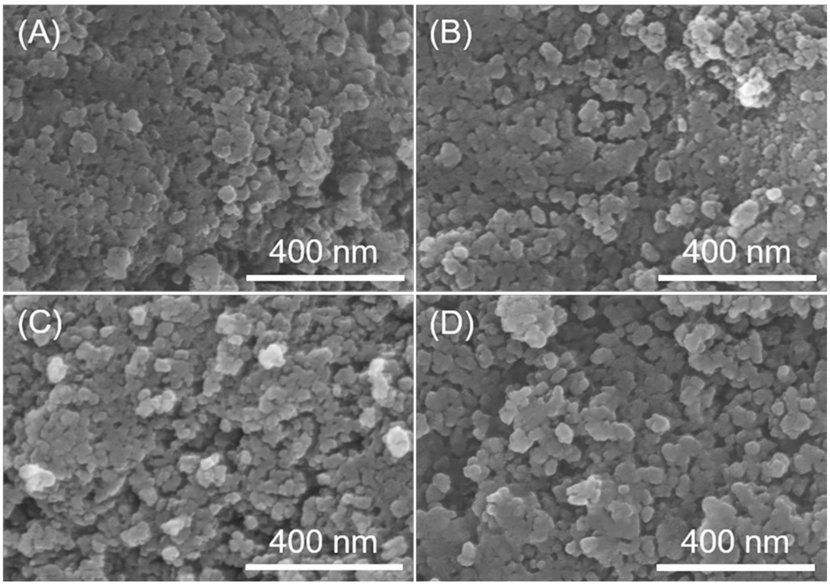

Fig. S2. SEM images of Pd/5CZA-yM catalysts. (A: Pd/5CZA-0M; B: Pd/5CZA-2M; C: Pd/5CZA-5M; D: Pd/5CZA-7M)

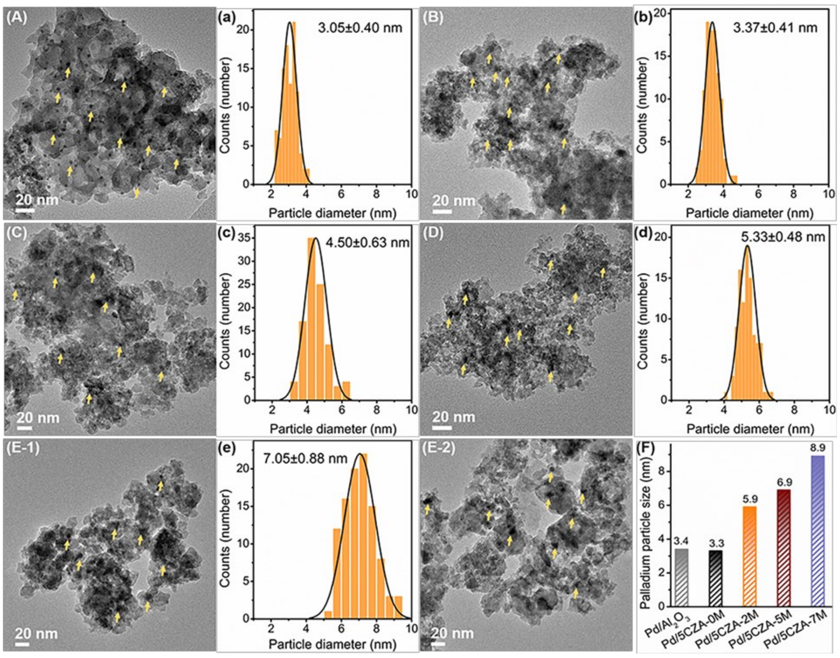

Fig. S3. TEM images and palladium particle's distribution of catalysts (A, a: Pd/Al_2O_3; B, b: Pd/5CZA-0M; C, c: Pd/5CZA-2M; D, d: Pd/5CZA-5M; E-1, E-2, e: Pd/5CZA-7M); the average palladium particle size of catalysts calculated from CO chemisorption (F).

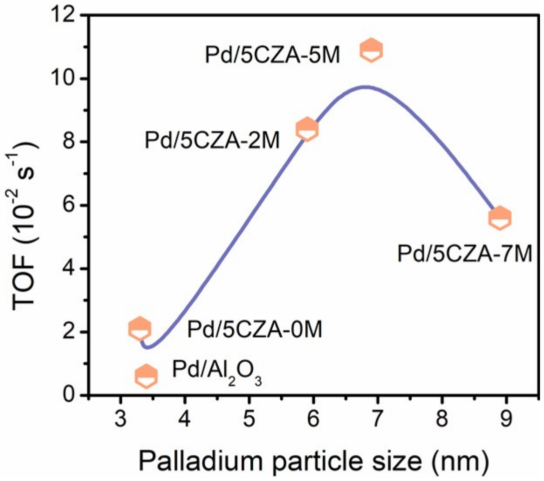

Fig. S4. Correlation of TOFs (at 285 ℃) of Pd/Al_2O_3 and Pd/5CZA-yM catalysts with the average palladium particle size calculated from CO chemisorption.

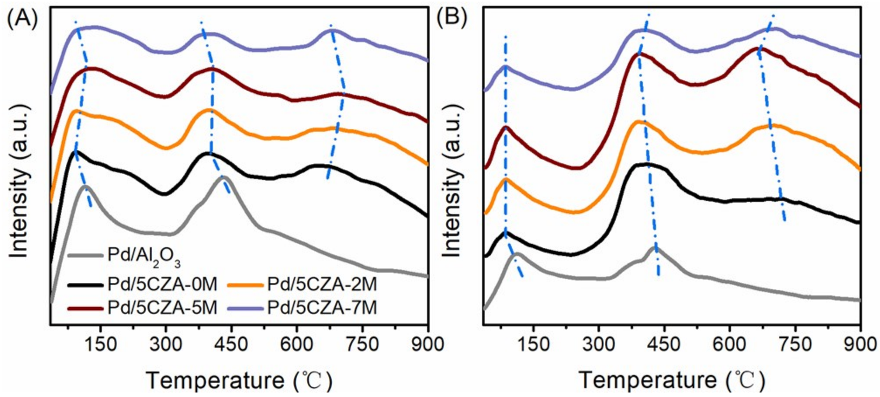

Fig. S5. NH_3-TPD (A) and CO_2-TPD (B) profiles of Pd/Al_2O_3 and Pd/5CZA-yM catalysts.

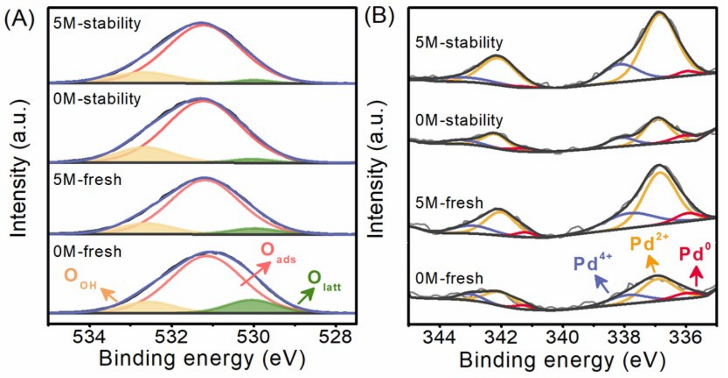

Fig. S6. The O 1s (A) and Pd 3d (B) XPS of fresh and used Pd/5CZA-0M and Pd/5CZA-5M catalysts. (used: after 60 h stability test at high onset conversion)

REFERENCE

1 W. Hu, G. Li, J. Chen, F. Huang, M. Gong, L. Zhong and Y. Chen, *Fuel*, 2017, **194**, 368-374.

2 M. Jeong, N. Nunotani, N. Moriyama and N. Imanaka, *Catal. Sci. Technol.*, 2017, **7**, 1986-1990.

3 K. Yasuda, T. Masui, T. Miyamoto and N. Imanaka, *J. Mater. Sci.*, 2011, **46**, 4046-4052.

4 R. Zhou, B. Zhao and B. Yue, *Appl. Surf. Sci.*, 2008, **254**, 4701-4707.

5 B. Yue, R. Zhou, X. Zheng and W. Lu, *Mater. Chem. Phys.*, 2009, **114**, 722-727.