Supplementary Information

Superior catalytic combustion of methane over Pd supported on oxygen vacancy-rich NiAl$_2$O$_4$

*Sha Li [ab#], Jie Li [b#], Zirui He [b], Yao Sheng [b], Wen Liu [*b]*

[1] Chemistry department, College of Chemistry and Materials Engineering, Zhejiang A & F University, Hangzhou 311300, China

[2] Scholl of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, Singapore 637459, Singapore

Section 1 Catalyst characterization procedures

H$_2$ and CH$_4$ temperature-programmed reduction (H$_2$-TPR and CH$_4$-TPR), O$_2$ temperature-programmed oxidation (O$_2$-TPO) and CO pulsed chemisorption experiments were performed on an Autochem II 2920 instrument equipped with a thermal conductivity detector. For H$_2$-TPR: 100 mg samples were treated in He gas at 300 °C for 0.5 h. After cooling to -50 °C, the samples were heated to 600 °C in 10 vol% H$_2$/Ar with a flow rate of 30 mL/min and a heating rate of 5 °C/min. As for CH$_4$-TPR: 100 mg catalysts were pretreated in He at 300 °C for 0.5 h, followed by cooling to 50 °C. Subsequently, the catalysts were heated to 500 °C in a mixture of 1 vol% CH$_4$/He at a heating rate of 5 °C /min. For O$_2$-TPO: 100 mg catalysts were heated to 900 °C and then cooled to 100 °C in a mixture of 1 vol% O$_2$/He, with a heating rate of 10 °C/min and a flow rate of 30 mL/min. The CO pulsed chemisorption experiments began by pretreating 100 mg of catalyst sample in 10% H$_2$/Ar (flow rate of 30 mL/min) at 300 °C for 2 h, followed by degassing at 350 °C in He gas for 30 min and subsequent cooling to 30 °C. Then, CO was introduced to the reduced samples every 2 min until saturation (i.e. no apparent CO uptake by the catalyst sample). The dispersion of Pd was estimated assuming a CO/Pd stoichiometry of 1:1. Pd particle sizes were estimated based on the Pd dispersion,

assuming spherical Pd particle shapes. *In situ* DRIFTS studies were performed on a Thermo Fisher IS50 FTIR spectrometer, equipped with an in situ diffuse reflectance reaction chamber and an MCT detector. In a typical measurement, ~30 mg of the sample was pretreated in 100 mL/min N_2 at 350 °C for 1 h to remove any surface impurities. The total reaction gas flow rate was 100 mL·min^{-1} with the same reaction gas composition of $CH_4 : O_2 : N_2 = 0.4 : 4 : 95.6$. The sample was then heated at 10 °C/min while multiple spectra were taken over a period of 0.5 h at each set point temperature (vuz, 200, 250, 300, 350 and 400 °C). Each in situ spectrum was the average of 64 scans with a spectral resolution of 4 cm^{-1}.

Section 2 Catalyst measurement procedures

The catalytic activity test was performed in a fixed-bed reactor. In a typical test, 100 mg of catalyst (40-60 mesh) was loaded into a quartz tube reactor and heated from room temperature to 550 °C with a rate of 5 °C·min^{-1}. GHSV (gas hourly space velocity) was kept at 180,000 mL·g^{-1}·h^{-1} for all experiments. The reaction gas contains CH_4 (2000 ppm) and 4 vol% O_2 (and 10 vol% H_2O in the wet condition) and using N_2 for dilution. The concentrations of CH_4 and CO_2 were detected by an Antaris IGS gas analyzer (Thermo Fisher). The turnover frequency (TOF) and apparent activation energy (E_a) were calculated at a methane conversion level below 20% in order to eliminate temperature gradient and transport limitations. The TOF is estimated according to:

TOF = N/(M × t)

Where TOF = moles of reactant per mole of Pd per second; N = number of moles of reactant, M = loading of Pd ×m_{cat} ×Pd(dispersion)/106.4, t = reaction time (s).

Additionally, T_{10}, T_{50}, and T_{90} were the reaction temperatures, which, corresponding to the conversions of CH_4 were 10, 50, and 90%, respectively.

Section 3 Eliminate the impact of internal diffusion

We excluded the influence of internal diffusion using the internal MTL method by

performing calculations based on the Weisz-Prater criterion. By approximating: $D_{eff} = \dfrac{\varepsilon D_M}{\tau}$

and $\dfrac{1}{\tau} = \varepsilon^2$, where D_{eff} is the effective diffusivity, D_M is the molecular diffusivity ($\sim 5.9 \times 10^{-5}$

m^2/s for CH_4 in air at 300 °C through extrapolation using the Chapman-Enskog theory), τ is

tortuosity and ε is the void faction of a catalyst pellet (~ 0.359 for close random packing). We

approximate the lower limit of D_{eff} to be $\sim 7.6 \times 10^{-6}$ m^2/s. Hence, the Weisz-Prater Criterion

is formulated as C $wp = \dfrac{r \cdot R^2}{C_s \cdot D_{eff}}$. In this context, the radius falls within the range of 1.5 to

2.1×10^{-4} meters. The mass of the catalyst is 0.1 grams, and its volume is 0.0404 millilitres,

respectively. The computed Cwp value, based on the Weisz-Prater criterion, is 0.12, which is

significantly below the threshold of 0.6. This indicates that the methane catalytic combustion

process is not hindered by internal diffusion limitations.

Furthermore, if the interfacial mass transfer were to impede the chemical reaction, the

fitting line on the Arrhenius plot would be expected to exhibit significant deviation from

certain data points. However, as depicted in Figure 6(b), such deviation is not observed.

Therefore, internal diffusion is not the decisive factor influencing the catalytic reaction

activity.

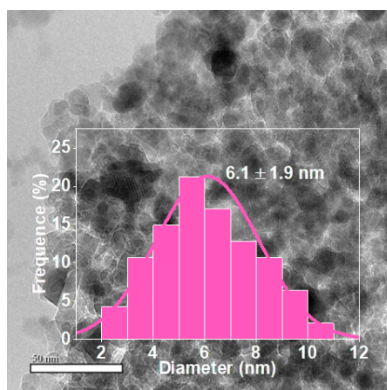**Figure S1** TEM image and particle size analysis of Pd/Ni$_{0.75}$Al$_{2.25}$O$_4$-900-550 catalyst.

Figure S2 In situ DRIFT spectra of $CH_4/O_2/N_2$ gas mixture adsorption $Pd/NiAl_2O_4$-100-550 at various temperatures for an adsorption time of 30 min.
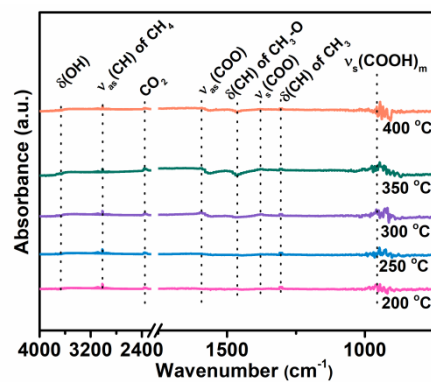
Figure S3 Light-curves for the fresh Pd/NiAl$_2$O$_4$-900-550 in wet feed gas.
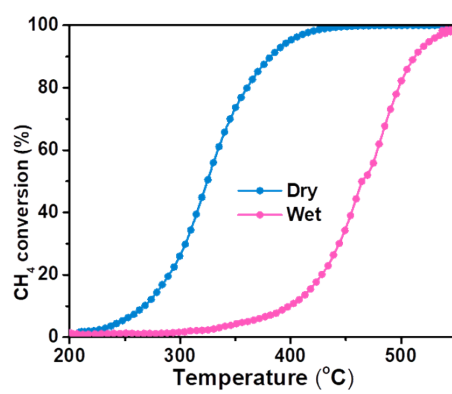
Table S1 Comparisons of performance of Pd-based catalysts prepared in the present work with other notable Pd based methane combustion catalysts reported in the literature.

catalysts	Pd wt.%	Feed gas composition	CH_4 GHSV $(ml \cdot g_{cat}^{-1} \cdot h^{-1})$	TOF (s^{-1}) /T (°C)	T_{50} (°C)	E_a $(kJ \cdot mol^{-1})$	Ref
Pd/NiAl$_2$O$_4$	1.0	0.2%CH$_4$, 4%O$_2$	360	0.052/300	325	58.8	This work
Pd/NiAl$_2$O$_4$-HTA[a]	1.0	0.2%CH$_4$, 4%O$_2$	360	-	396	-	This work
Pd@CeO$_2$/Al$_2$O$_3$	1.0	0.5%CH$_4$, 20%O$_2$	1000	-	320	103.0	(1)
Pd/H-ZSM-5	1.0	1%CH$_4$, 20%O$_2$	300	-	300	84.7	(2)
Pd/SiO$_2$	1.0	0.3%CH$_4$, 2.4%O$_2$	300	-	355	84	(3)
Pd/MgAl$_2$O$_4$	1.0	0.2%CH$_4$, 4%O$_2$	360	0.043/300	372	50.1	(4)
Pd@ZSM-5		1%CH$_4$, 5%O$_2$	600	-		70.7	(5)
Pd-La/Al$_2$O$_3$	1.0	0.5%CH$_4$, 5%O$_2$	90	-	375		(6)
Pd/Al$_2$O$_3$	1.0	0.2%CH$_4$, 0.4%O$_2$	240	0.01/330	350	124	(7)
Pd/Al$_2$O$_3$-HTA[b]	1.0	0.2%CH$_4$, 4%O$_2$	360	-	483	-	(4)
Pd/MgAl$_2$O$_4$-HTA[b]	1.0	0.2%CH$_4$, 4%O$_2$	360	-	420	-	(4)

[a,b] The catalysts were hydrothermally treated in 10 vol% H_2O at 750 °C for 10 h.

Table S2. The PdO particle size of the catalysts.

Samples	PdO particle size (nm)[a]	Pd loading [b] (wt%)	PdO particle size (nm) [c]
Pd/Ni$_{0.75}$Al$_{2.25}$O$_4$-850-550	7.3	-	6.1
Pd/NiAl$_2$O$_4$-900-700	11.8	1.01	10.7
Pd/NiAl$_2$O$_4$-900-850	18.0	-	15.6

[a] Determined the Scherrer equation using the XRD diffraction peak at 33.8°.

[b] Analyzed by ICP-AES.

[c] Measured by TEM.

Table S3 Summary of the catalytic activity of the catalysts.

Samples	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)
Pd/Ni$_{0.75}$Al$_{2.25}$O$_4$-850-550	288	345	442
Pd/NiAl$_2$O$_4$-900-550	268	325	380
Pd/NiAl$_2$O$_4$-900-700	307	397	503
Pd/NiAl$_2$O$_4$-900-850	333	422	523

References

(1) M. Cargnello, J.J. Delgado Jaen, J.C. Hernandez Garrido, K. Bakhmutsky, T. Montini, J.J. Calvino Gamez, R.J. Gorte, P. Fornasiero, *Science*, 2012, **337**, 713-717.
(2) Y. Lou, J. Ma, W. Hu, Q. Dai, L. Wang, W. Zhan, Y. Guo, X. M. Cao, Y. Guo, P. Hu, G. Lu, *Acs Catal.*, 2016, **6**, 8127-8139.
(3) A.M. Venezia, G. Di Carlo, G. Pantaleo, L.F. Liotta, G. Melaet, N. Kruse, *Appl. Catal. B-Environ.*, 2009, **88**, 430-437.
(4) J. Li, Y. Zhang, W.P. Shan, H. He, *Fuel*, 2023, **340**, 127493.
(5) M.Y. Gao, Z.M. Gong, X.F. Weng, W.X. Shang, Y.C. Chai, W.L. Dai, G.J. Wu, N.J. Guan, L.D. Li, *Chinese J. Catal.*, 2021, **42**, 1689-1699.
(6) X.B. Wang, X.Q. Zhang, M.M. Cao, X.F. Wang, Q.W. Gao, C.B. Deng, X. Huang, *Energ. Fuel*, 2022, **36**, 6999-7005.
(7) J.J. Chen, J.W. Zhong, Y. Wu, W. Hu, P.F. Qu, X. Xiao, G.C. Zhang, X. Liu, Y. Jiao, L. Zhong, Y.Q. Chen, *Acs Catal.*, 2020, **10**, 10339-10349.