

# Supplementary Materials

## **Stable performance of supported PdO<sub>x</sub> catalyst on mesoporous silica-alumina of water tolerance for methane combustion under wet conditions**

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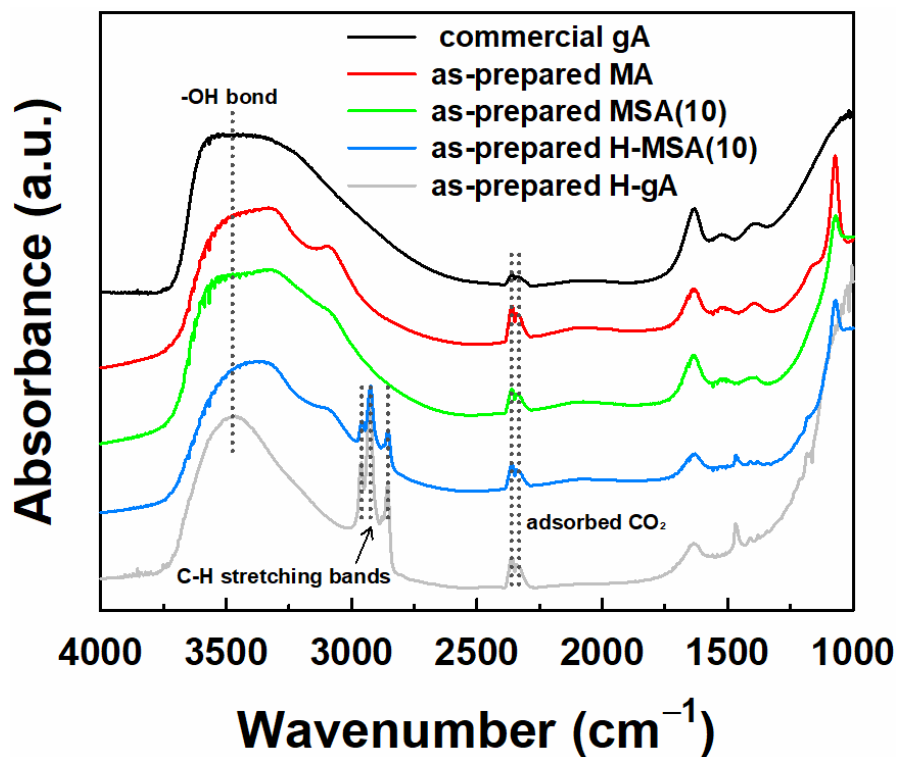
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Number of Pages: 10, Number of Figures: 8, Number of Tables: 1

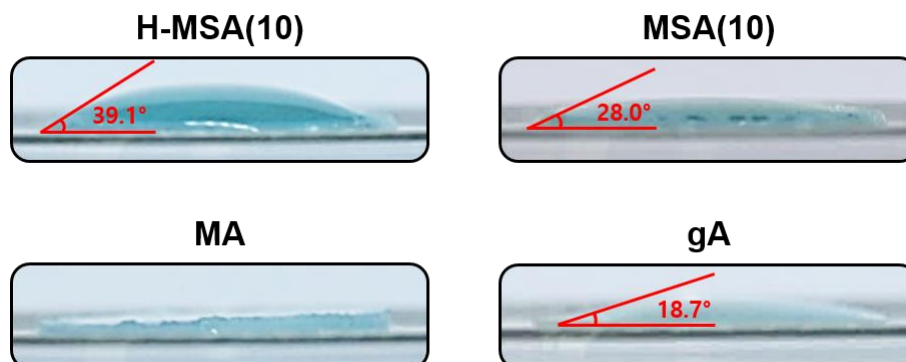
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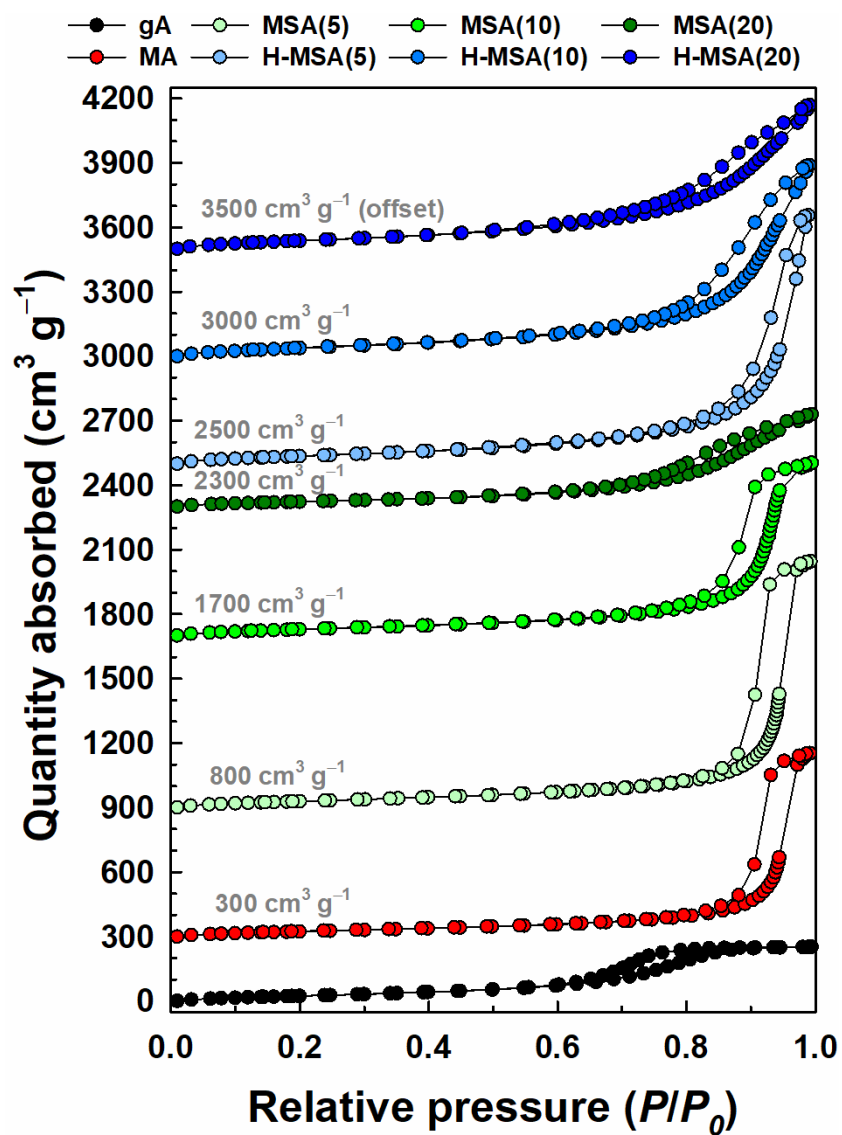
<sup>†</sup>The authors contributed equally to this work.



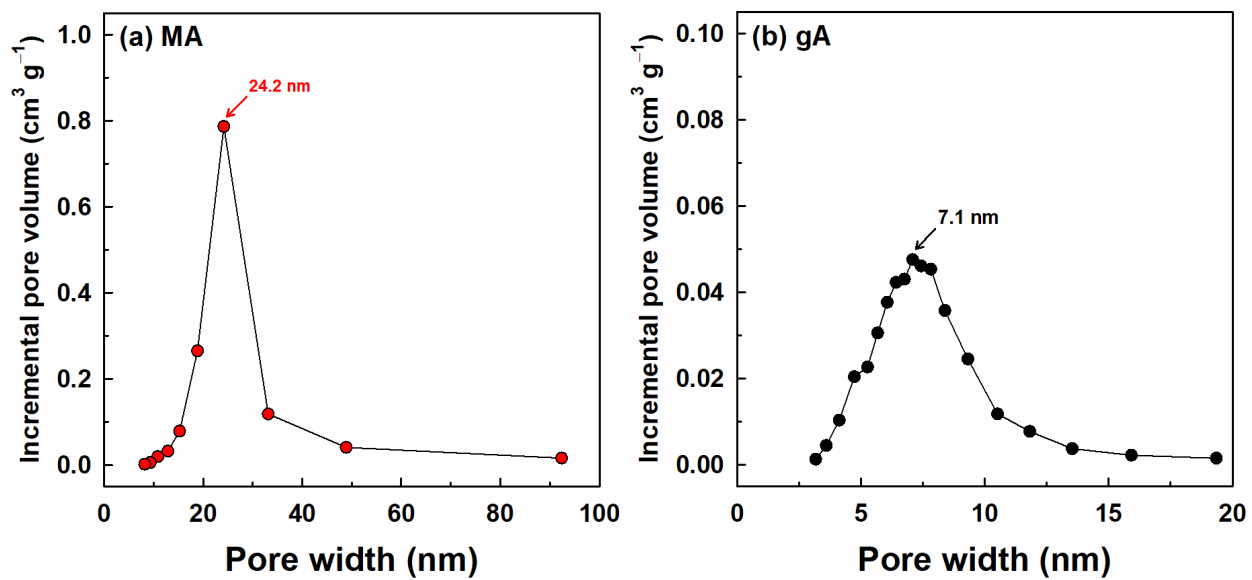
**Figure S1.** FT-IR spectra of the as-synthesized samples (H-MSA(10), MSA(10), MA and gA) and water-tolerant  $\gamma$ -alumina (H-gA).



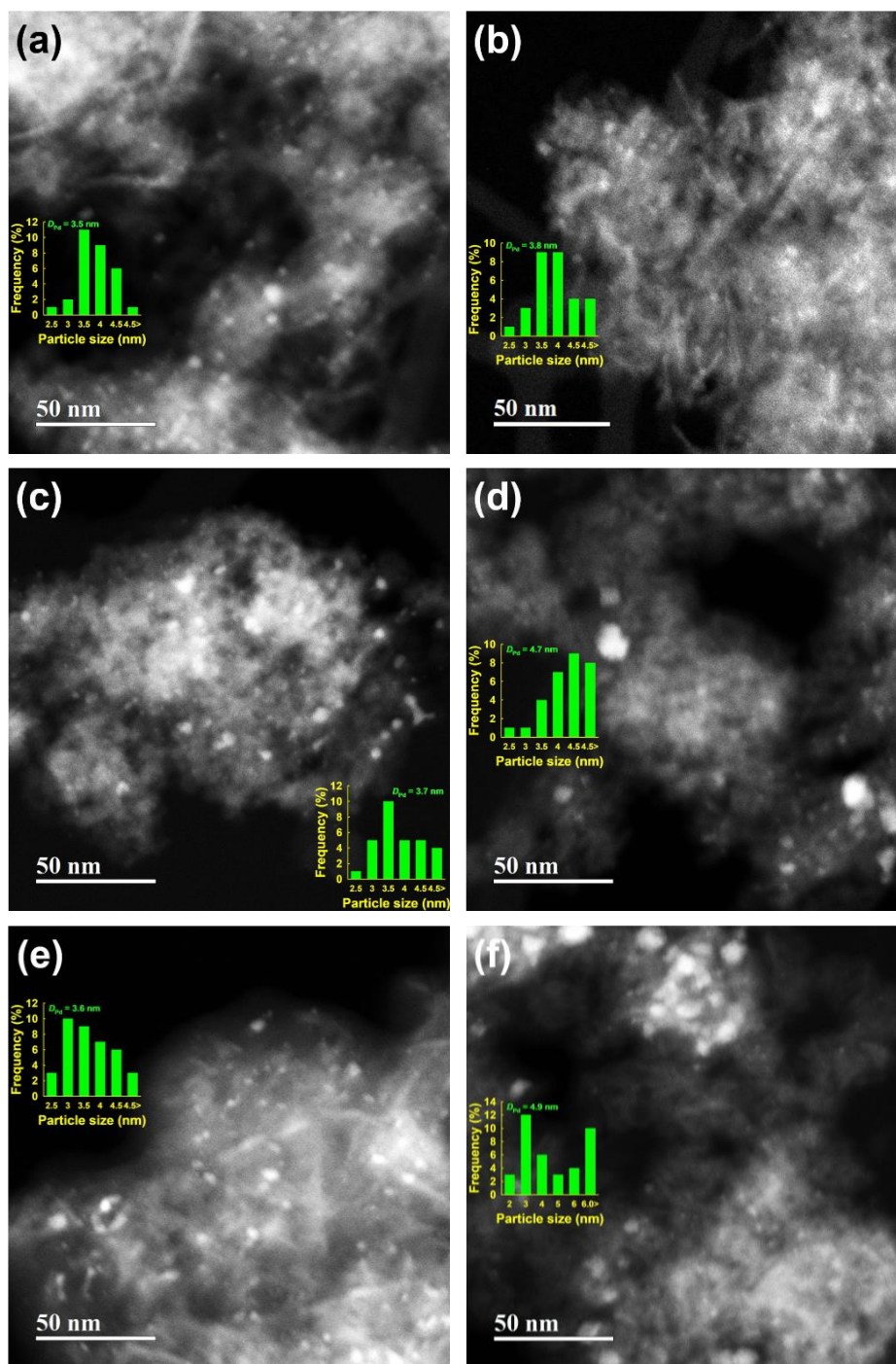
**Figure S2.** Wettability experiments with H-MSA(10), MSA(10), MA, and gA. The measured contact angle is added into each panel except MA showing the spreading behavior.



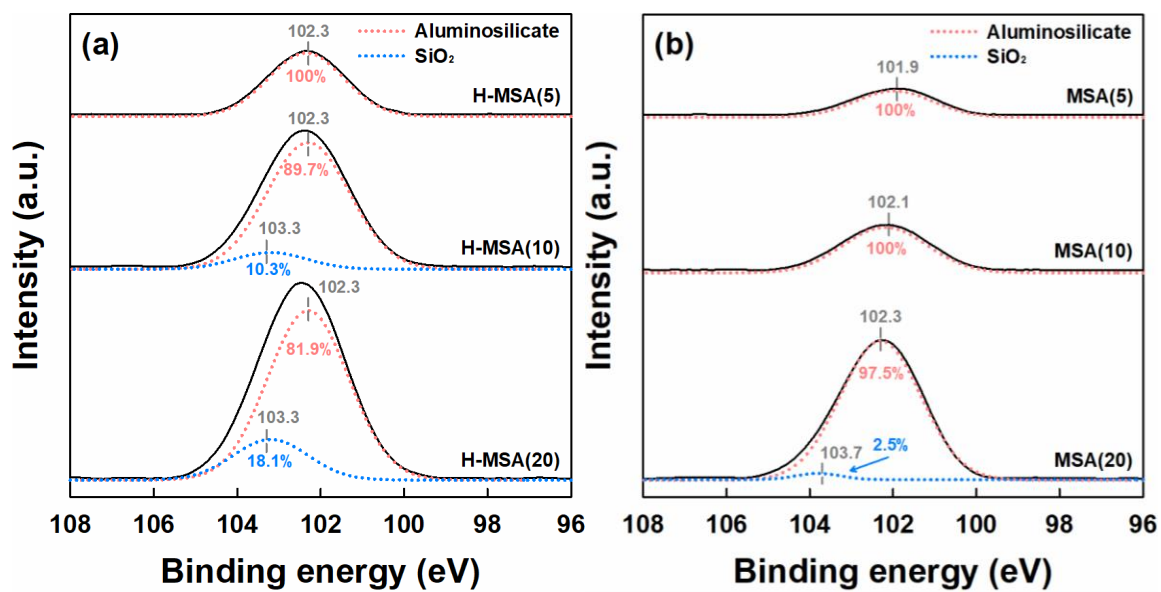
**Figure S3.**  $\text{N}_2$  adsorption-desorption isotherms of the prepared support materials.



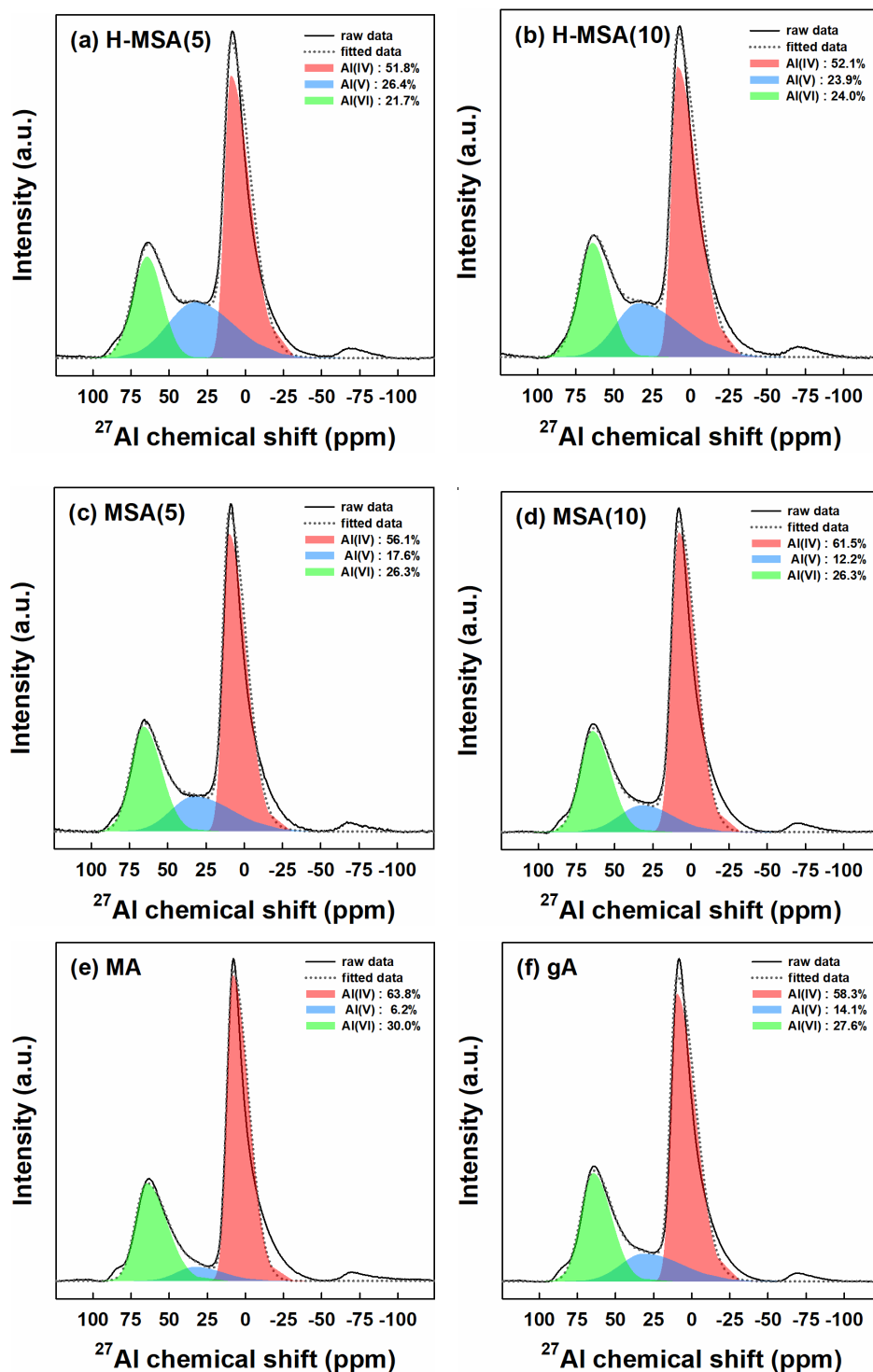
**Figure S4.** Pore size distribution curves of the prepared support materials: (a) MA and (b) gA.



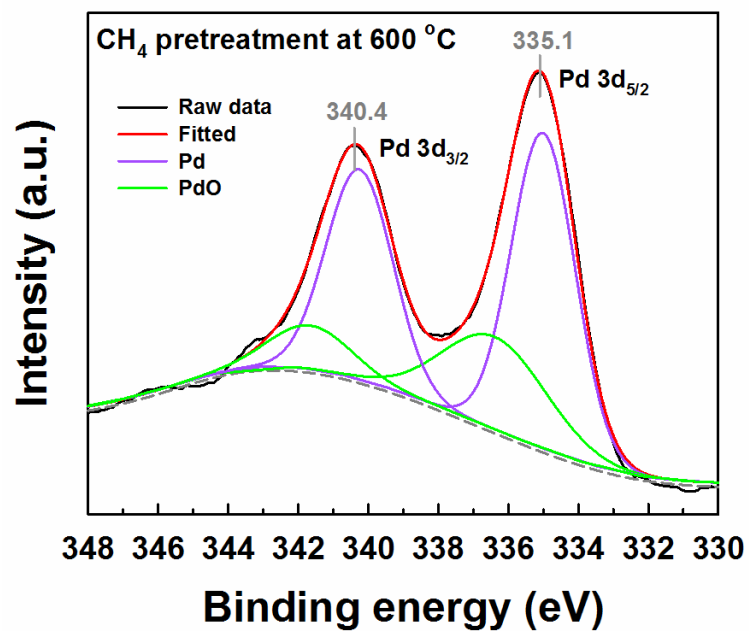
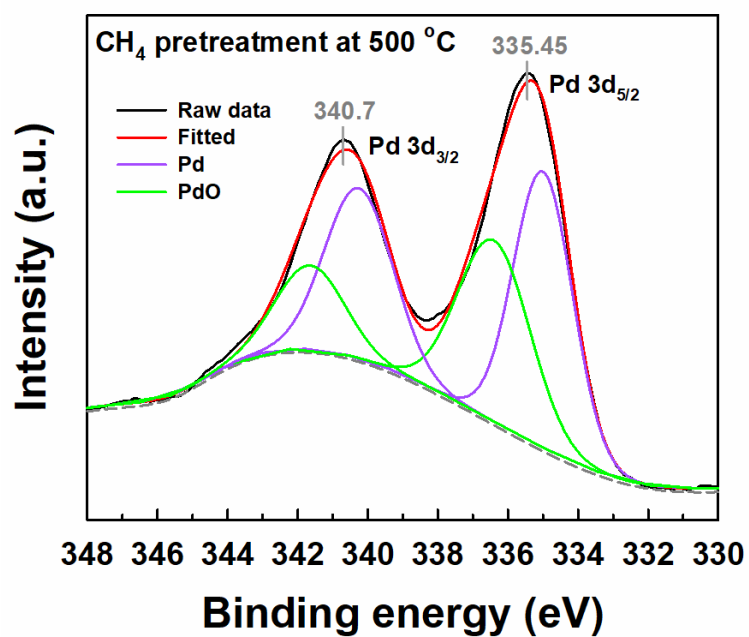
**Figure S5.** TEM images of (a) the fresh PdO<sub>x</sub>/H-MSA(10), (b) spent PdO<sub>x</sub>/H-MSA(10), (c) fresh PdO<sub>x</sub>/MSA(10), (d) spent PdO<sub>x</sub>/MSA(10), (e) fresh PdO<sub>x</sub>/MA, and (f) spent PdO<sub>x</sub>/MA. The spent samples were obtained after isothermal test at 500 °C for 24 h. Insets represent the particle size distribution of PdO<sub>x</sub> determined by statistical analysis of ca. 30–40 white particles.



**Figure S6.** XPS results of (a) H-MSA( $x$ ) and (b) MSA( $x$ ) in the binding energy region of Si 2p.



**Figure S7.**  $^{27}\text{Al}$  MAS NMR spectra of all supports: (a) H-MSA(5), (b) H-MSA(10), (c) MSA(5), (d) MSA(10), (e) MA and (f) gA (red: octahedral  $\text{Al}^{\text{VI}}$ ; blue: penta-coordinated  $\text{Al}^{\text{V}}$ ; green: tetrahedral  $\text{Al}^{\text{IV}}$ ). The fitting results are marked by gray dots.



**Figure S8.** XPS spectra of the catalyst samples pretreated with 20% CH<sub>4</sub> in N<sub>2</sub> at 500 and 600 °C.

**Table S1.** Isothermal methane combustion performance of the reported Pd catalysts and PdO<sub>x</sub>/H-MSA(5) in this work

Catalyst	Feed composition				GHSV (cm <sup>3</sup> g <sup>-1</sup> h <sup>-1</sup> )	Temp. (°C)	CH <sub>4</sub> conv. (%)	Ref.
	CH <sub>4</sub>	O <sub>2</sub>	H <sub>2</sub> O	Balance				
	(%)	(%)	(%)	gas				
<b>Pd/κ-CZ</b>	1	20	5	N <sub>2</sub>	30,000	330	60	[1]
<b>Pd2Ce</b>	0.07	8.5	10	N <sub>2</sub>	36,000	425	65	[2]
<b>Al-Pd/MA-A72</b>	0.5	10	10	N <sub>2</sub>	40,000	500	95	[3]
<b>0.6Pd@S-1</b>	1	16	4.5	N <sub>2</sub>	50,000	410	95	[4]
<b>Pd/5CZA-5M</b>	1	5	5	N <sub>2</sub>	50,000	360	50	[5]
<b>Pd/Na-MOR-Dno</b>	1	4	5	N <sub>2</sub>	70,000	410	92	[6]
<b>1.1Pd-SSZ-13(16)</b>	0.15	5	10	He	100,000	400	99	[7]
<b>Pd/TS-1</b>	0.7	-	3–4	air	100,000	400	92	[8]
<b>PdCe</b>	0.5	2	10	He	180,000	450	55	[9]
<b>PdCe SCS</b>	0.5	2	10	He	200,000	450	50	[10]
<b>Pd/ZrO<sub>2</sub>(85)</b>	0.1	3.15	10	N <sub>2</sub>	240,000	500	95	[11]
<b>Pd/ZrO<sub>2</sub>(700)</b>	0.1	3.15	10	N <sub>2</sub>	240,000	450	97.5	[12]
<b>PdO<sub>x</sub>/H-MSA(5)</b>	0.4	12	5	N <sub>2</sub>	200,000	500	98	This work

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