Table S1. The content of phosphorus of P modified supports.

Supports	Synthesis Method	The Load of P (wt.%)
0Pθ-Al_2O_3	-	0
0.1Pθ-Al_2O_3	incipient wetness impregnation	0.11
0.3Pθ-Al_2O_3		0.31
0.6Pθ-Al_2O_3		0.6
1Pθ-Al_2O_3		1.02
1.5Pθ-Al_2O_3		1.43
3Pθ-Al_2O_3		2.67

Table S2. The specific surface area and pore volume of the supports.

Supports	S_{BET} ($m^2 \cdot g^{-1}$)	Percentage of Decline Relative to θ-Al_2O_3	Volume ($cm^3 \cdot g^{-1}$)	Percentage of Decline Relative to θ-Al_2O_3
0Pθ-Al_2O_3	111.44	0.0	0.442	0.0
0.1Pθ-Al_2O_3	111.08	0.3	0.438	1.0
0.3Pθ-Al_2O_3	105.74	4.3	0.424	4.3
0.6Pθ-Al_2O_3	103.93	6.7	0.413	6.6
1Pθ-Al_2O_3	103.49	7.1	0.413	6.6
1.5Pθ-Al_2O_3	102.63	7.9	0.395	10.6
3Pθ-Al_2O_3	100.41	9.9	0.371	16.1

Table S3. Quantitative results of TGA test of supports.

Supports	The Amount of Desorbed Water (mmol·g^{-1})
0Pθ-Al_2O_3	1.49
0.1Pθ-Al_2O_3	1.18
0.3Pθ-Al_2O_3	1.33
0.6Pθ-Al_2O_3	1.37
1Pθ-Al_2O_3	1.60
1.5Pθ-Al_2O_3	1.63
3Pθ-Al_2O_3	1.87

Table S4. Quantitative results of NH_3-TPD test of supports.

Sample	Peak1 Temperature (°C)	Amounts of NH_3 Desorption at Peak1 (umol·g^{-1})	Relative Surface Hydroxyl Density (1)
0Pθ-Al_2O_3	152	116.28	1.00
0.1Pθ-Al_2O_3	156	91.57	0.79
0.3Pθ-Al_2O_3	158	95.17	0.82
0.6Pθ-Al_2O_3	154	109.16	0.94
1Pθ-Al_2O_3	155	127.12	1.09
1.5Pθ-Al_2O_3	152	139.77	1.20
3Pθ-Al_2O_3	154	211.03	1.82

(1) Relative surface hydroxyl density: the surface hydroxyl density of θ-Al_2O_3 was set as 1, and the relative values of other samples with respect to θ-Al_2O_3 were defined as the relative surface hydroxyl density of the support.

Table S5. Binding energy of P 2p.

Supports	P 2p Binding Energy (eV)
0.1Pθ-Al_2O_3	—
0.3Pθ-Al_2O_3	133.1
0.6Pθ-Al_2O_3	133.34
1Pθ-Al_2O_3	133.6
1.5Pθ-Al_2O_3	133.8
3Pθ-Al_2O_3	134.0
PO_4^{3-}	130.2
HPO_4^{2-}	133.4
$H_2PO_4^-$	133.8

Table S6. Element content of Pd catalysts.

Samples	Content of P (wt.%)	Content of Pd (wt.%)
Pd/0Pθ-Al_2O_3	0	0.79
Pd/0.1Pθ-Al_2O_3	0.11	0.81
Pd/0.3Pθ-Al_2O_3	0.31	0.80
Pd/0.6Pθ-Al_2O_3	0.6	0.82
Pd/1Pθ-Al_2O_3	1.02	0.78
Pd/1.5Pθ-Al_2O_3	1.43	0.81
Pd/3Pθ-Al_2O_3	2.67	0.82

Table S7. Quantitative results of TGA test of samples.

Samples	The Amount of Desorbed Water (mmol/g)
Pd/0Pθ-Al_2O_3	1.69
Pd/0.1Pθ-Al_2O_3	0.95
Pd/0.3Pθ-Al_2O_3	1.33
Pd/0.6Pθ-Al_2O_3	1.59
Pd/1Pθ-Al_2O_3	1.80
Pd/1.5Pθ-Al_2O_3	1.92
Pd/3Pθ-Al_2O_3	2.05

Table S8. Quantitative results of NH_3-TPD test of samples.

Samples	Peak1 Temperature (°C)	The Desorption of NH_3 at Peak 1 (umol/g)	Relative Surface Hydroxyl Density
Pd/0Pθ-Al_2O_3	154	120.67	1.000
Pd/0.1Pθ-Al_2O_3	160	78.13	0.647
Pd/0.3Pθ-Al_2O_3	156	97.95	0.812
Pd/0.6Pθ-Al_2O_3	151	110.29	0.914
Pd/1Pθ-Al_2O_3	148	124.31	1.030
Pd/1.5Pθ-Al_2O_3	148	136.45	1.131
Pd/3Pθ-Al_2O_3	148	198.10	1.642

Table S9. Apparent activation energy of samples in the presence 8% water.

Samples	Apparent Activation Energy (kJ·mol^{-1})
Pd/0Pθ-Al_2O_3	172.81
Pd/0.1Pθ-Al_2O_3	170.24
Pd/0.3Pθ-Al_2O_3	171.14
Pd/0.6Pθ-Al_2O_3	170.41
Pd/1Pθ-Al_2O_3	172.07
Pd/1.5Pθ-Al_2O_3	172.05
Pd/3Pθ-Al_2O_3	177.60

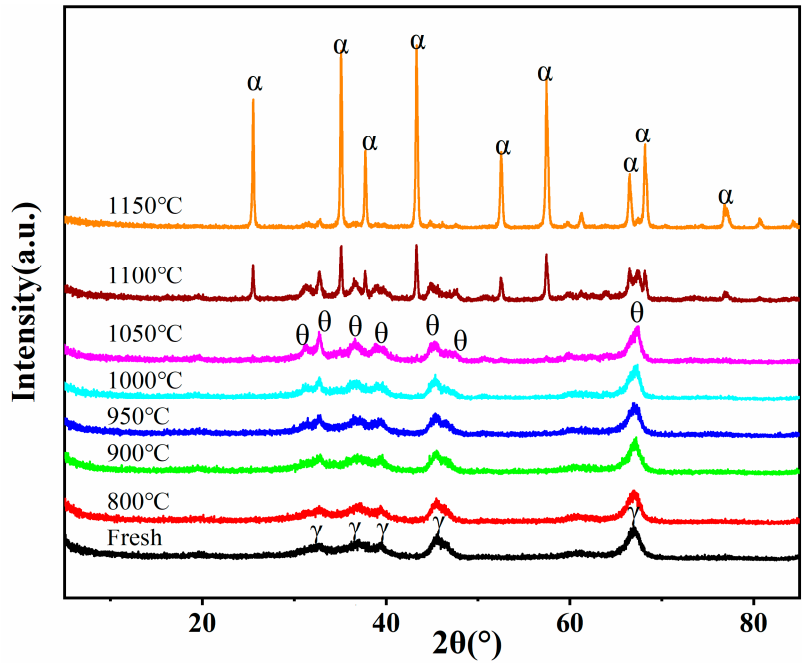

Figure S1. XRD patterns of the commercial γ-Al_2O_3 calcined at different temperature.

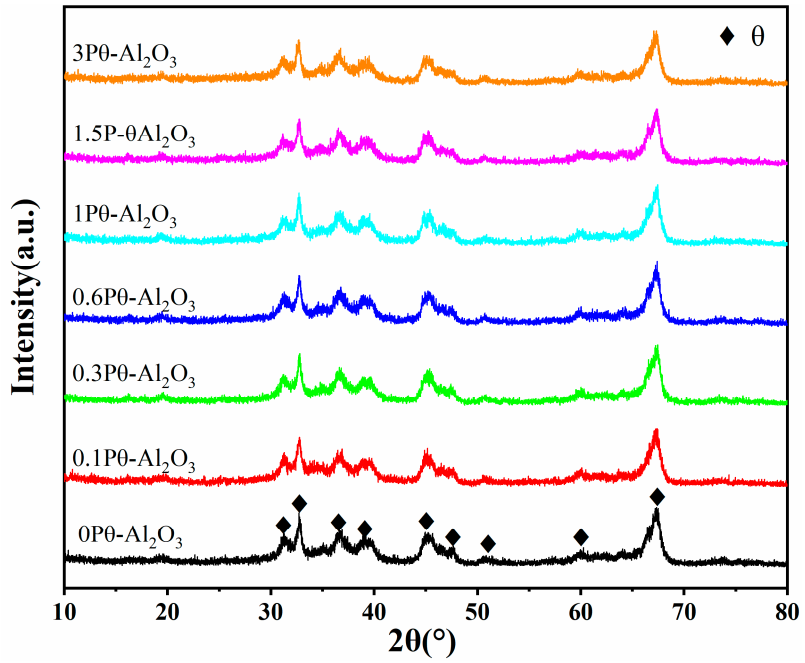

Figure S2. XRD patterns of the xPθ-Al_2O_3 supports.

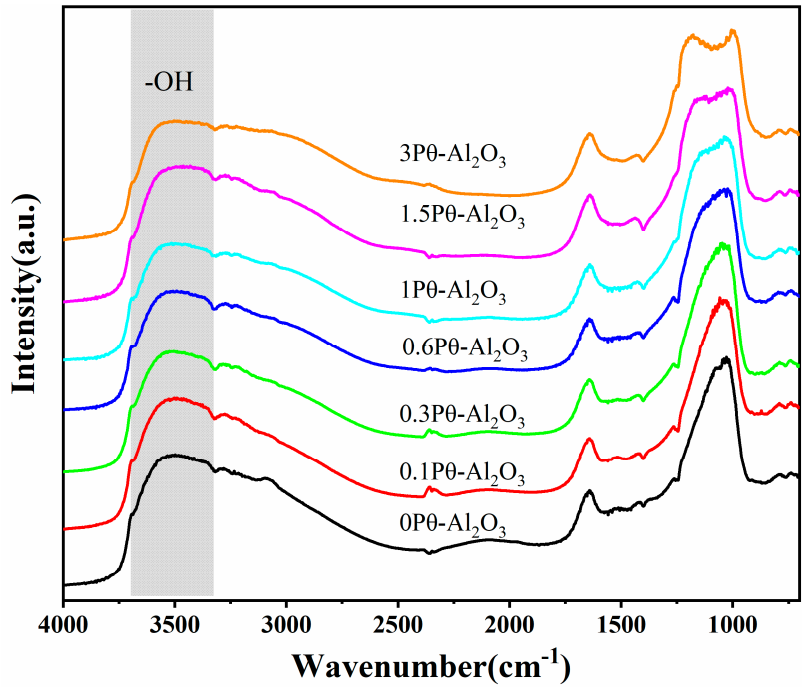

Figure S3. FT-IR profiles of supports.

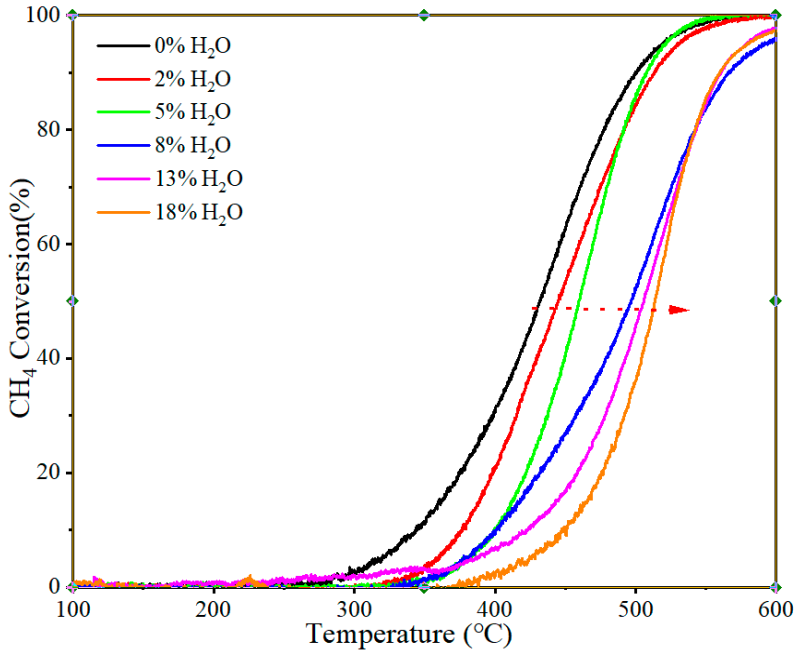

Figure S4. Catalytic combustion of methane over Pd/γ-Al2O3 with different amounts of water Conditions: 2000ppmCH4, 5 vol.% O2, 0–18 vol.%H2O , N2 balance; GHSV=36,000 h^{-1}.

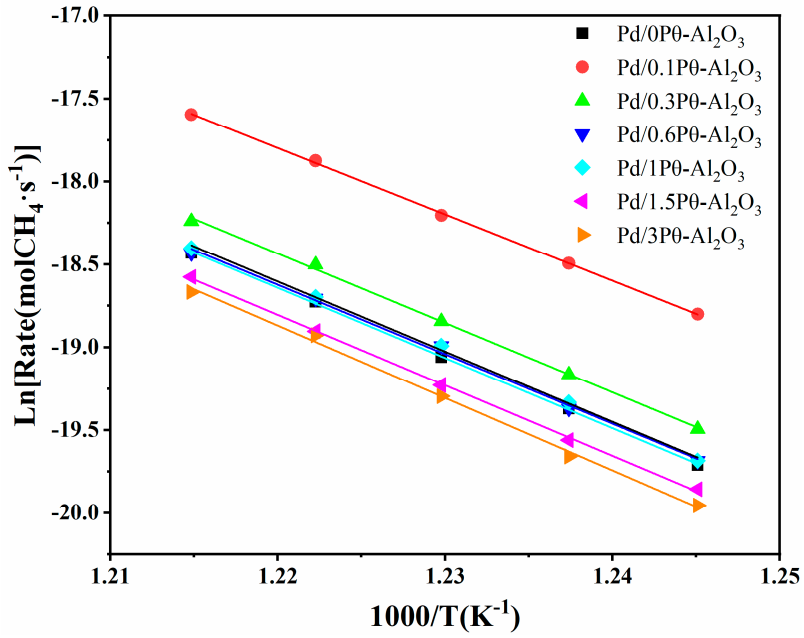

Figure S5. The Arrhenius curve of the samples in the presence of 8% water. (Conditions: 2000ppm CH_4, 5%O_2, 8%H_2O and N_2 as balance gas, GHSV=180,000h^{-1}).