

## ***Supplementary Information***

# Selective Catalytic NO<sub>x</sub> Reduction by H<sub>2</sub> in Excess O<sub>2</sub> over Pt/Zirconium Phosphate Nanosheet.

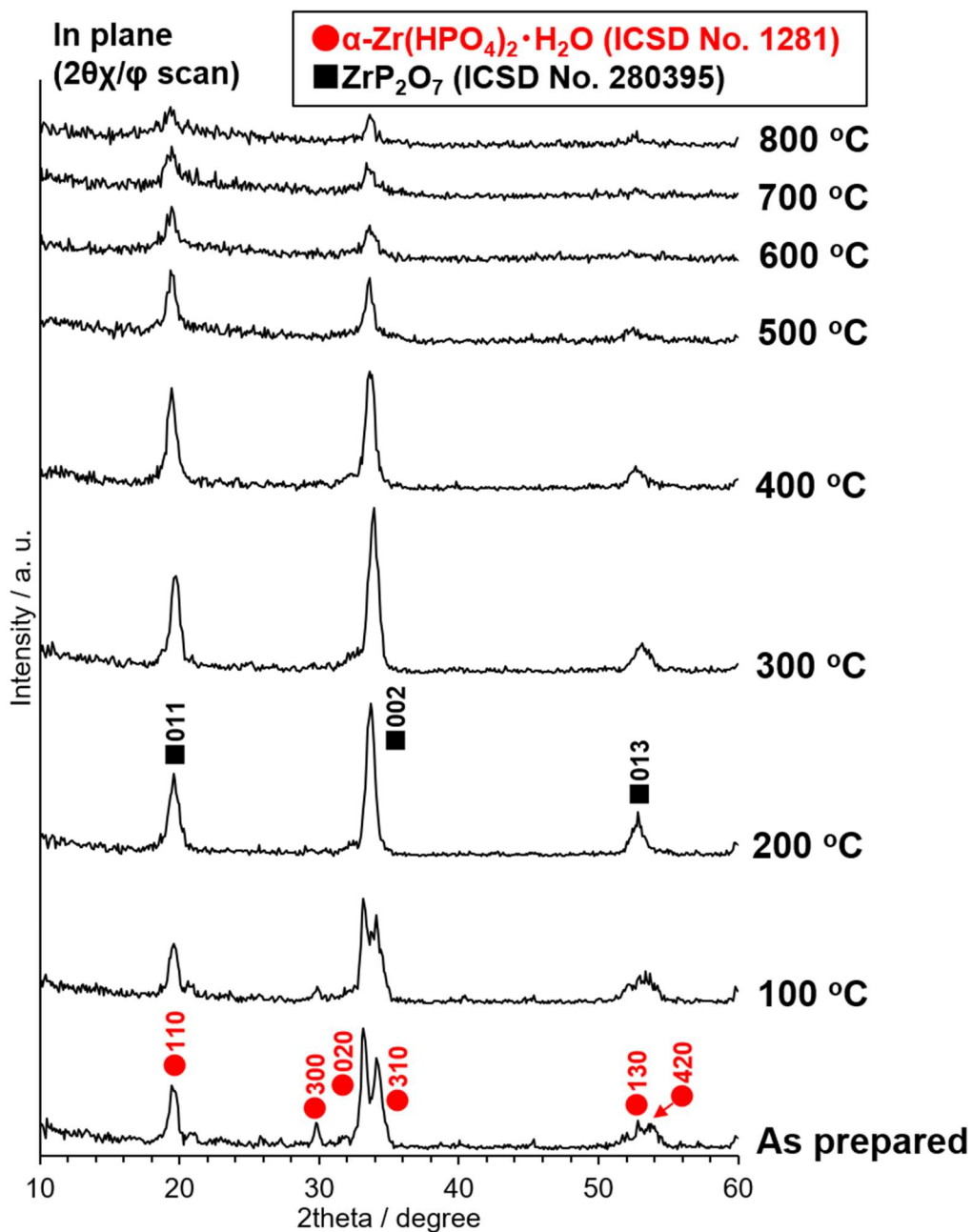
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a) Faculty of Advanced Science and Technology, Kumamoto University; 2-39-1, Kurokami, Chuo-ku, Kumamoto, 860-8555, Japan.

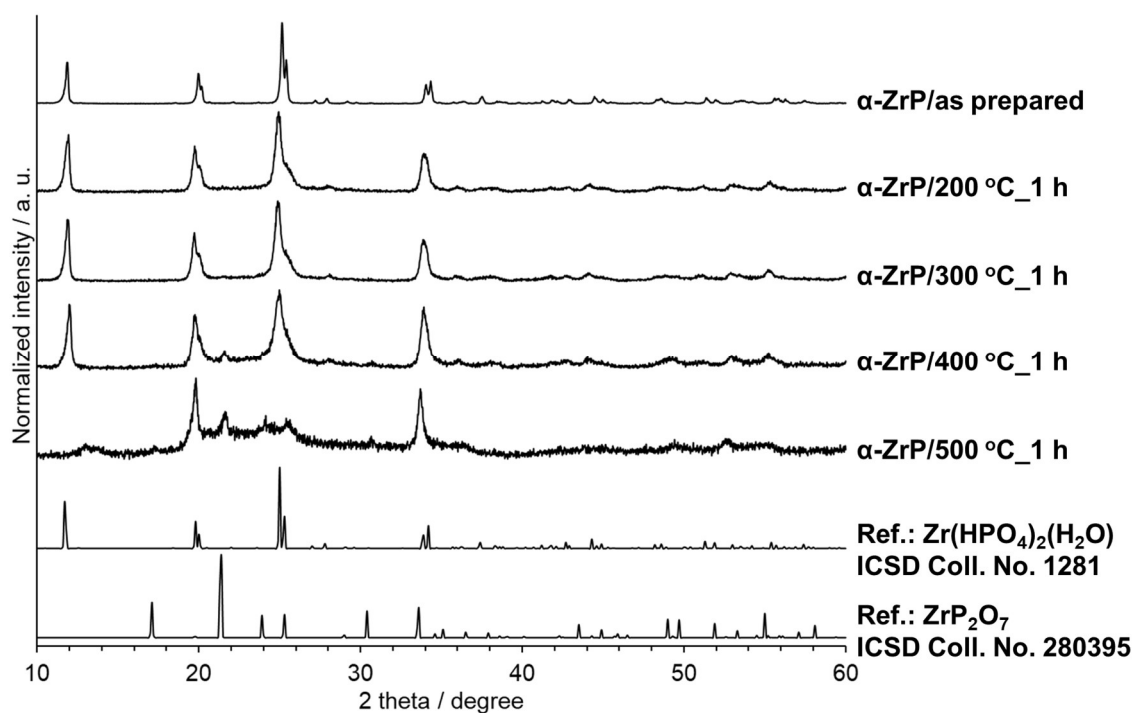
b) Graduate School of Science and Technology, Kumamoto University; 2-39-1, Kurokami, Chuo-ku, Kumamoto, 860-8555, Japan.

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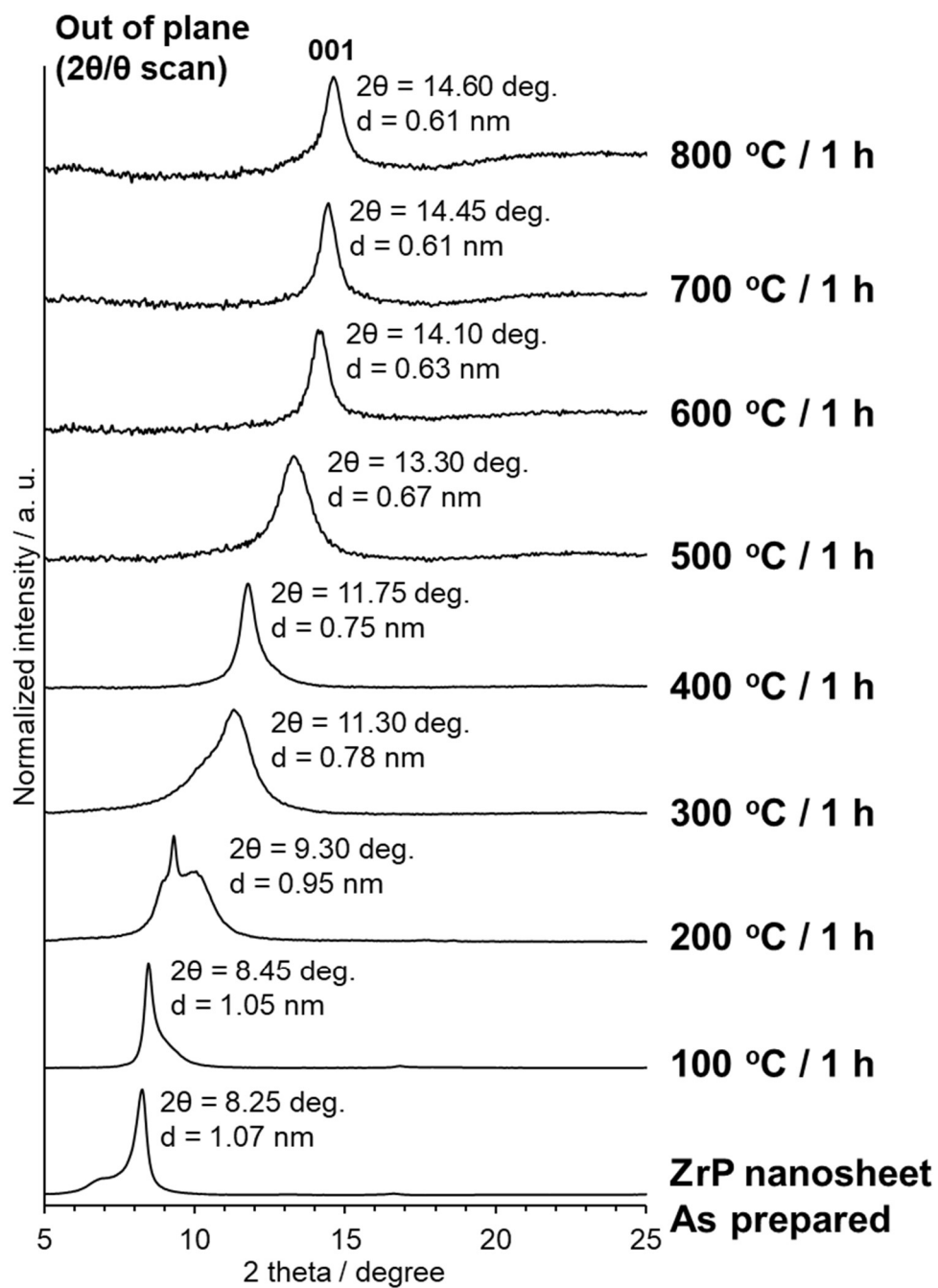
d) Institute of Industrial Nanomaterials (IINa), Kumamoto University; 2-39-1, Kurokami, Chuo-ku, Kumamoto, 860-8555, Japan.



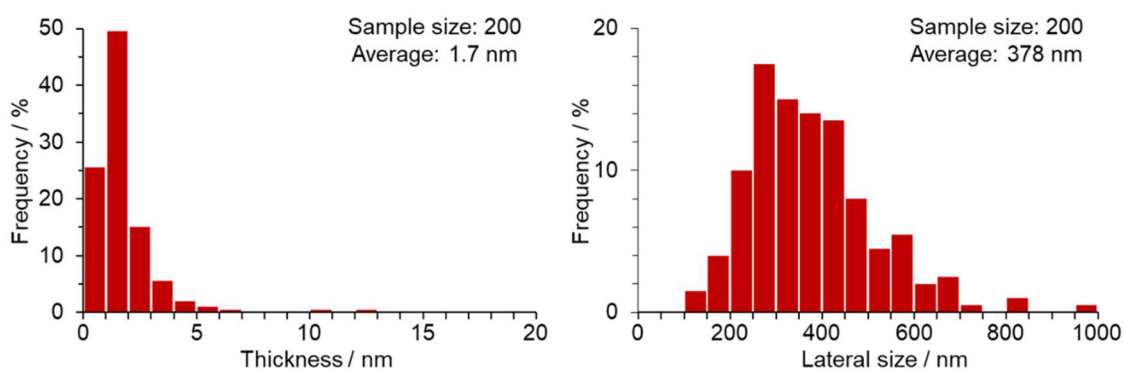
**Figure S1.** In-plane XRD patterns ( $2\theta/\varphi$  scan) of the ZrP nanosheet spin-coating film deposited on a Si wafer before and after annealing at 100-800 °C for 1 h.



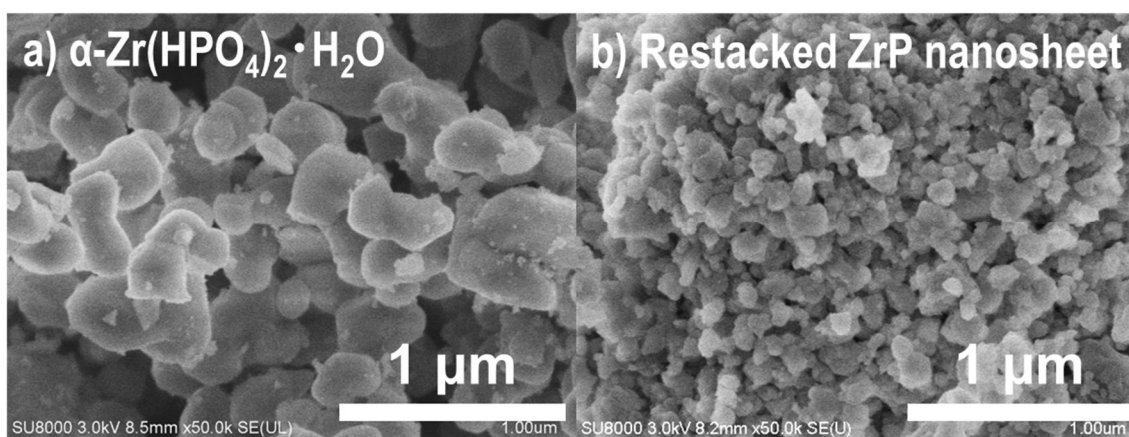
**Figure S2.** Powder XRD patterns ( $2\theta/\theta$  scan) of the  $\alpha$ -ZrP ( $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O) before and after annealing at 200-500 °C for 1 h, ICSD #1281 ( $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O), and ICSD #280395 (ZrP<sub>2</sub>O<sub>7</sub>).



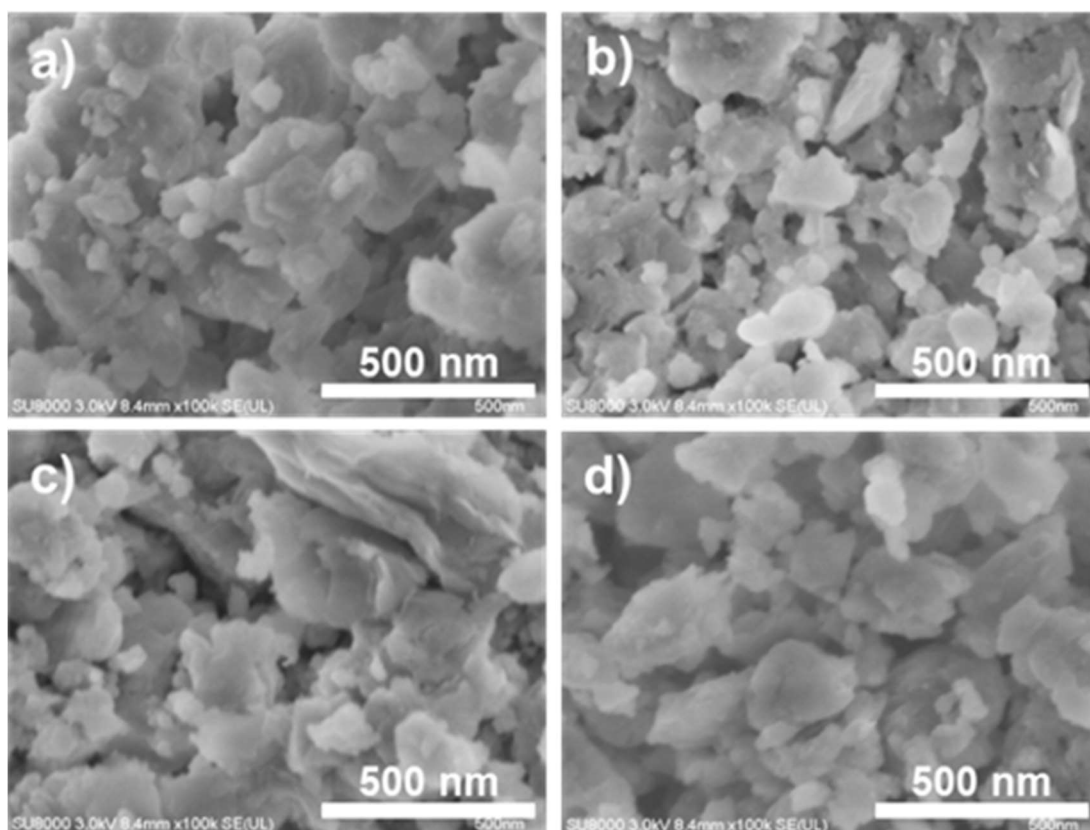
**Figure S3.** Out-of-plane XRD patterns (2 $\theta$ / $\theta$  scan) of the ZrP nanosheet spin-coating film deposited on a Si wafer before and after annealing at 100-800 °C for 1 h.



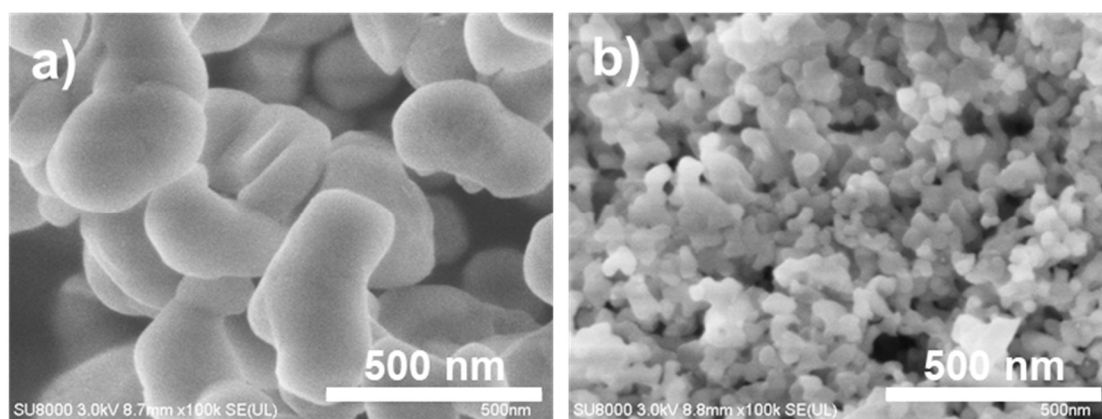
**Figure S4.** Thickness and lateral size distributions of the ZrP nanosheet deposited on a Si wafer (analysis of AFM images).



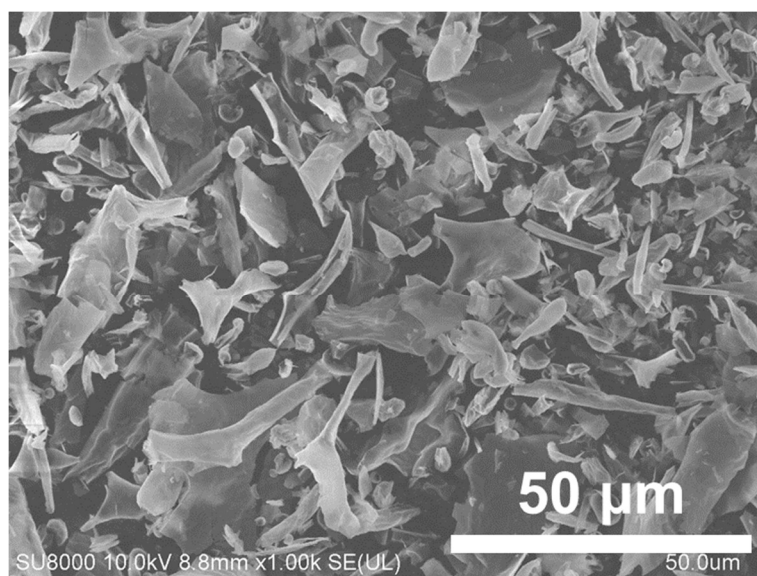
**Figure S5.** FE-SEM images of the (a)  $\alpha$ -ZrP ( $\alpha$ -Zr( $\text{HPO}_4$ ) $_2 \cdot \text{H}_2\text{O}$ ) and (b) restacked ZrP nanosheet.



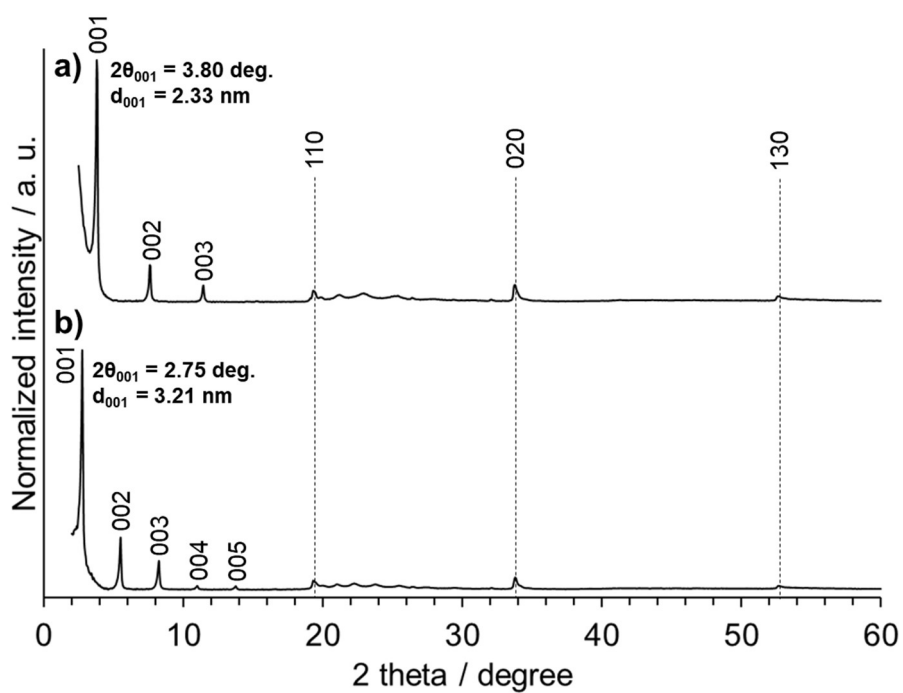
**Figure S6.** FE-SEM images of (a) 0.08, (b) 0.14, (c) 0.22, and (d) 0.49 wt% Pt (ads.)/ZrP nanosheet.



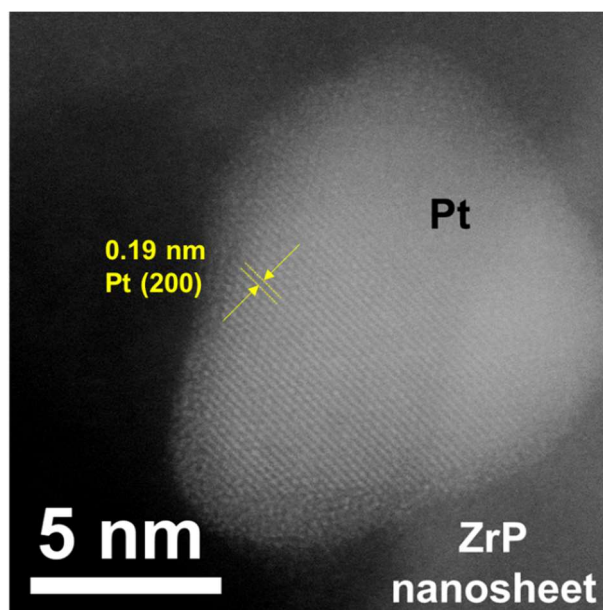
**Figure S7.** FE-SEM images of the (a) 0.5 wt% Pt (ads.)/ $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and (b) 0.4 wt% Pt (ads.)/ZrP<sub>2</sub>O<sub>7</sub>.



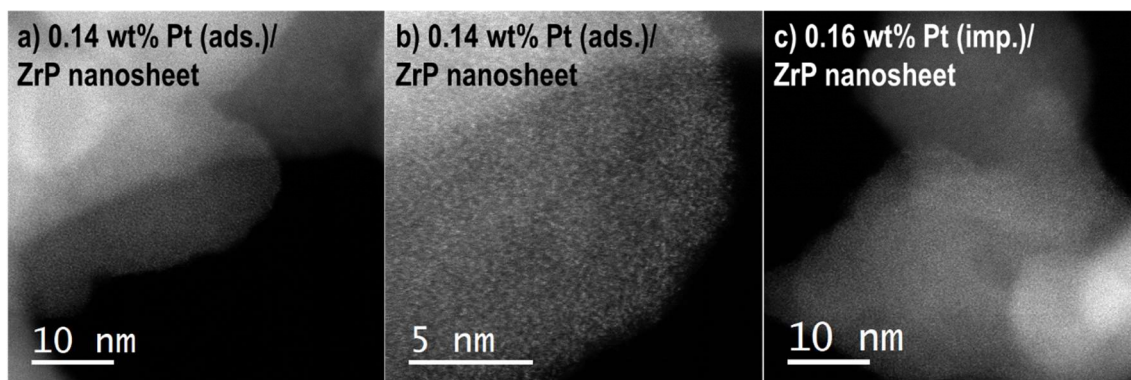
**Figure S8.** FE-SEM image of the freeze-dried ZrP nanosheet.



**Figure S9.** Powder XRD patterns ( $2\theta/\theta$  scan) of the (a) hexylamine (HA)- and the (b) decylamine (DA)-restacked ZrP nanosheet.

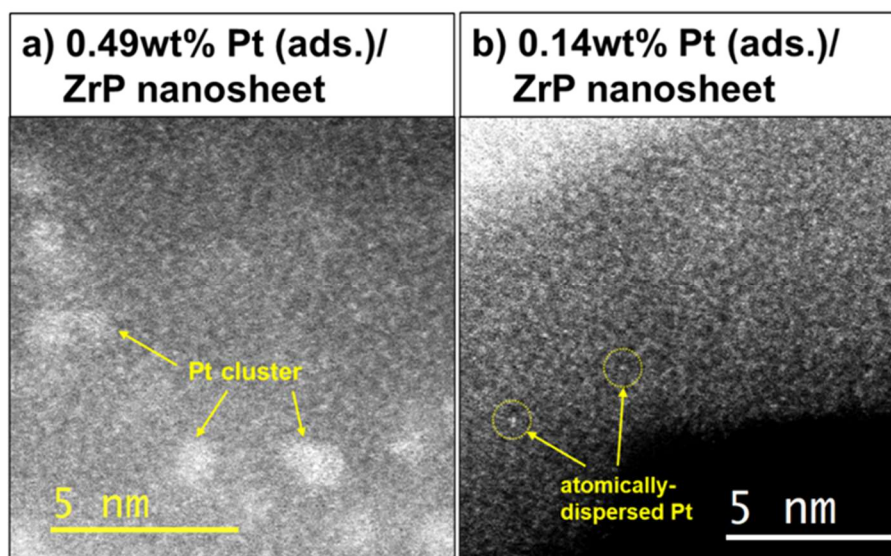


**Figure S10.** A HAADF-STEM image of the Pt (particle size  $\sim 14$  nm) particle on ZrP nanosheet (0.49 wt% Pt (ads.)/ZrP nanosheet).

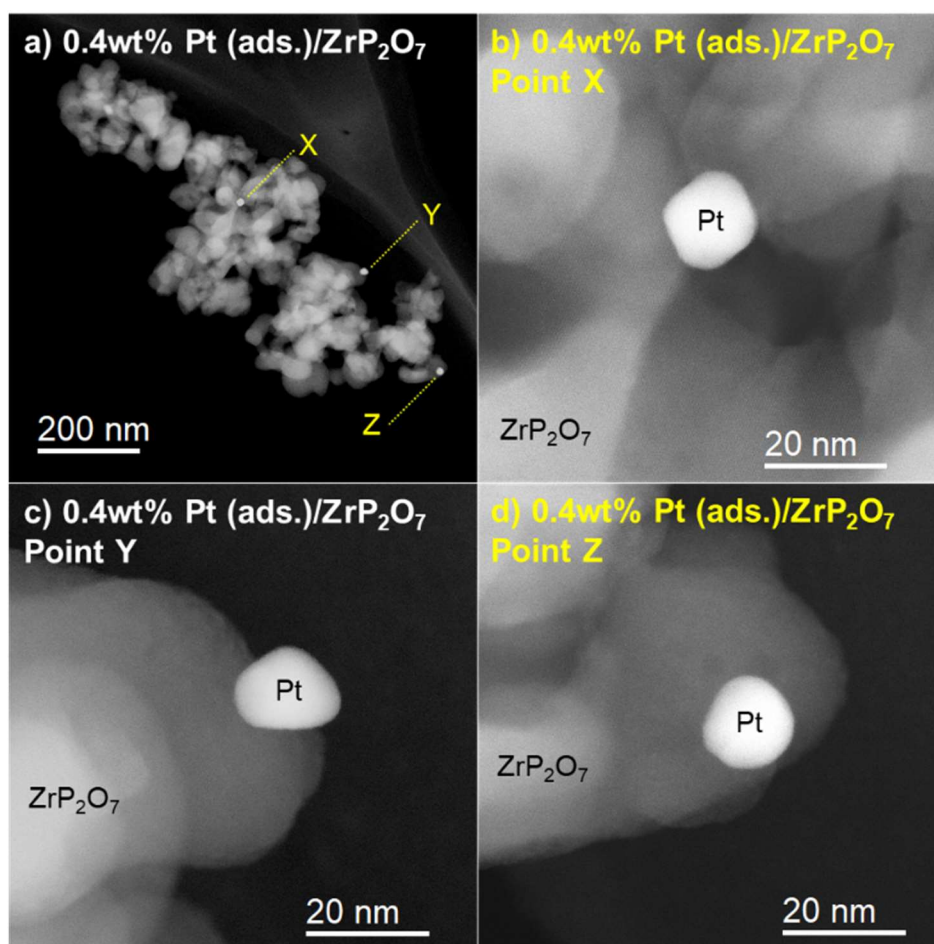


**Figure S11.** HAADF-STEM images of the (a-b) 0.14 wt% Pt (ads.)/ZrP nanosheet and (c) 0.16 wt% Pt (imp.)/ZrP nanosheet.

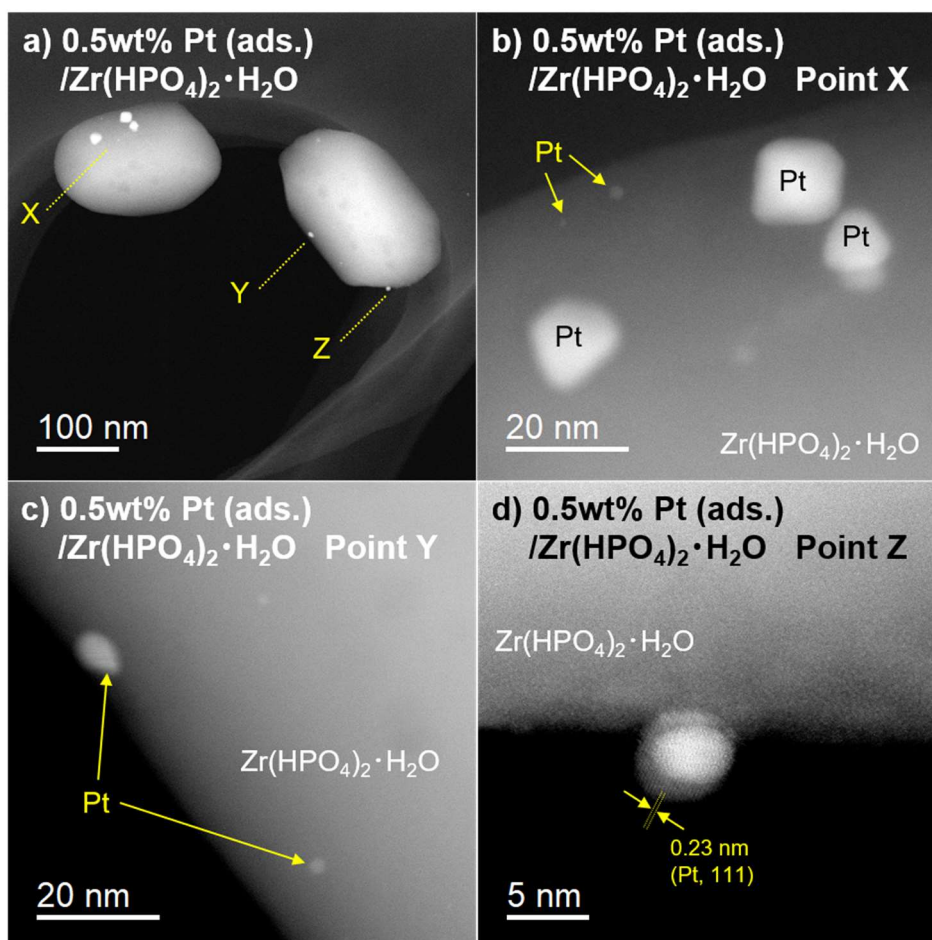




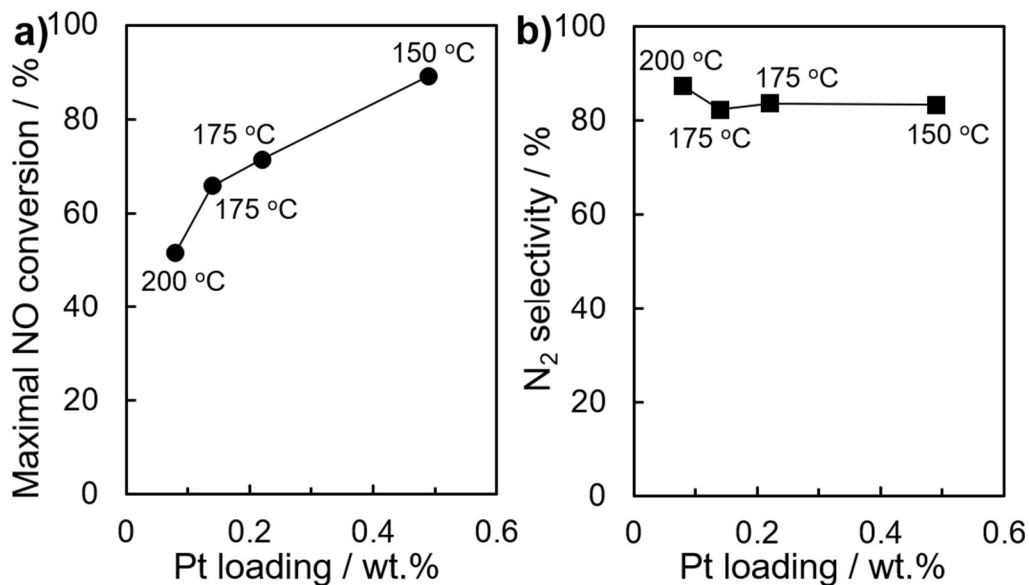
**Figure S12.** HAADF-STEM images showing Pt clusters and atomically-dispersed Pt on (a) 0.49 wt% Pt (ads.)/ZrP nanosheet and (b) 0.14 wt% Pt (ads.)/ZrP nanosheet.



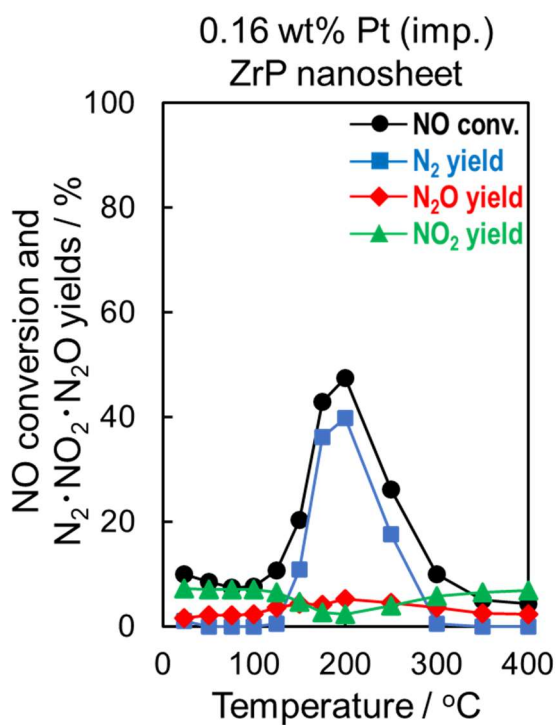
**Figure S13.** (a-d) HAADF-STEM images of 0.4 wt% Pt (ads.)/ZrP<sub>2</sub>O<sub>7</sub>. The images (b), (c), and (d) are zoomed images of the area marked by X, Y, and Z in (a).



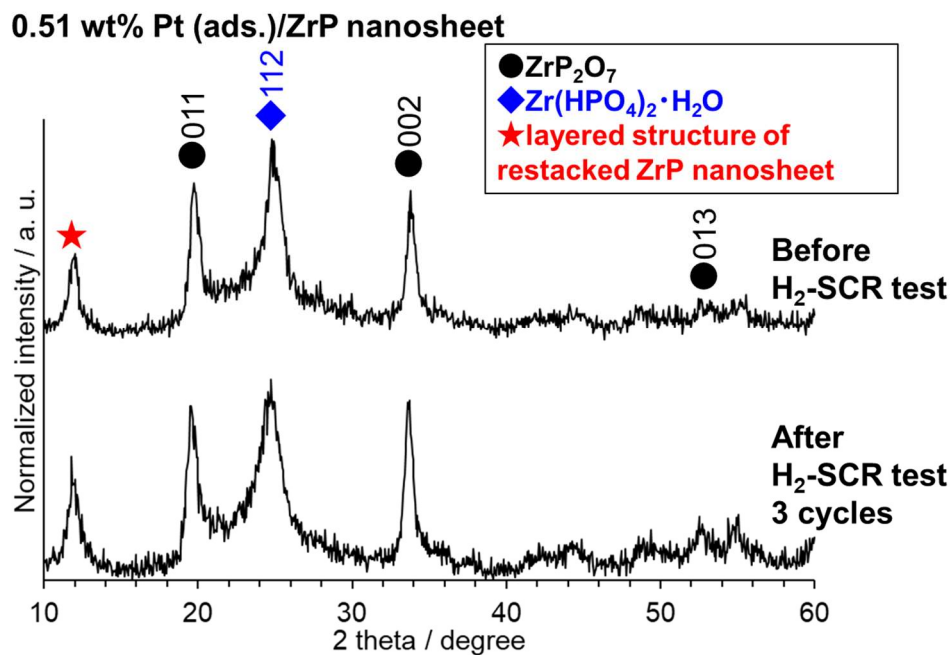
**Figure S14.** (a-d) HAADF-STEM images of 0.5 wt% Pt (ads.)/ $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. The images (b), (c), and (d) are zoomed images of the area marked by X, Y, and Z in (a).



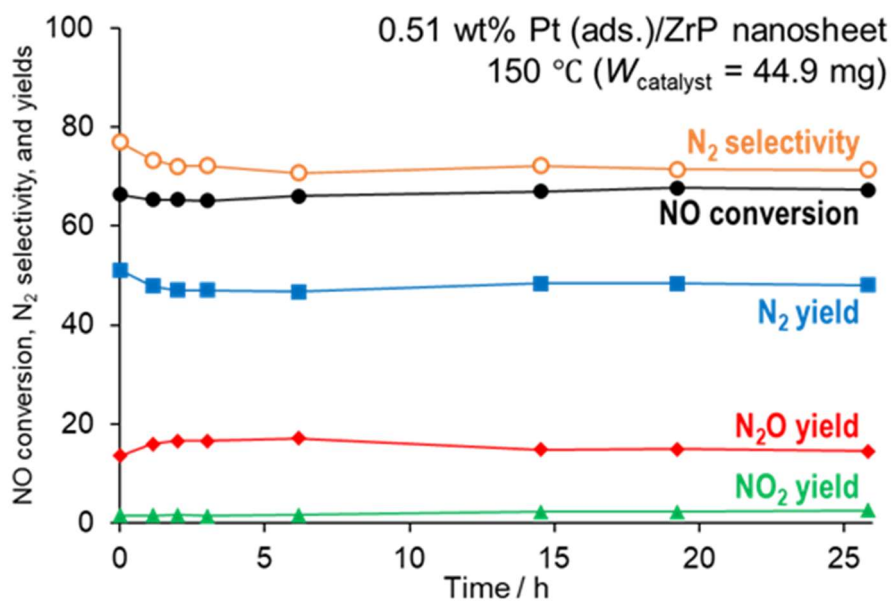
**Figure S15.** (a) Maximal NO conversion for H<sub>2</sub>-SCR over 0.08 (200 °C), 0.14 (175 °C), 0.22 (175 °C), and 0.49 wt% (150 °C) Pt (ads.)/ZrP nanosheet. (b) N<sub>2</sub> selectivity over 0.08-0.49 wt% Pt (ads.)/ZrP nanosheet at the same temperatures for (a).



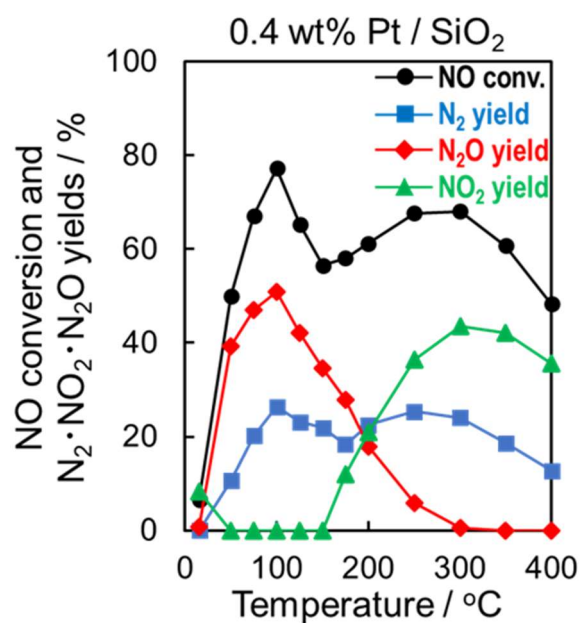
**Figure S16.** Temperature dependence of NO conversion and product yields over 0.16 wt% Pt (imp.)/ZrP nanosheet. NO (200 ppm), H<sub>2</sub> (5,000 ppm), O<sub>2</sub> (10%), and He balance.



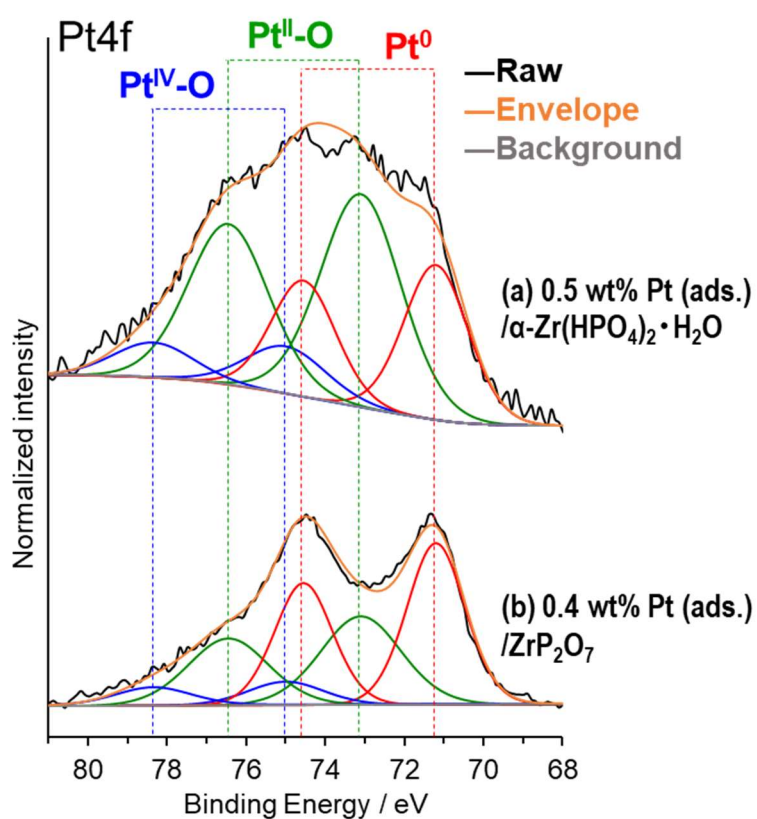
**Figure S17.** Powder XRD patterns ( $2\theta/\theta$  scan) of the 0.51 wt% Pt (ads.)/ZrP nanosheet before and after examining 3 cycles of  $\text{H}_2$ -SCR performance test.



**Figure S18.** Continuous  $\text{H}_2$ -SCR performance test over 0.51 wt% Pt (ads.)/ZrP nanosheet at 150 °C in NO (200 ppm),  $\text{H}_2$  (5,000 ppm),  $\text{O}_2$  (10%), and He balance ( $W_{\text{catalyst}} = 44.9$  mg).



**Figure S19.** Temperature dependence of NO conversion and product yields over 0.4 wt% Pt/SiO<sub>2</sub>. NO (200 ppm), H<sub>2</sub> (5,000 ppm), O<sub>2</sub> (10%), and He balance.



**Figure S20.** Pt 4f XPS spectra of 0.5 wt% Pt (ads.)/α-Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and 0.4 wt% Pt (ads.)/ZrP<sub>2</sub>O<sub>7</sub>. The intensity was normalized using the maximal intensity of Zr3d spectra.

**Table S1.** BET specific surface area ( $S_{\text{BET}}$ ) of the  $\alpha$ -ZrP ( $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O) and its derivatives.

Samples	$S_{\text{BET}}$ / m <sup>2</sup> /g
$\alpha$ -ZrP (as prepared)	13.2
Restacked ZrP nanosheet (0.1 M HCl)	26.1
Freeze-dried ZrP nanosheet	12.4
HA-intercalated ZrP nanosheet (400 °C/1 h/air)	40.0
DA-intercalated ZrP nanosheet (400 °C/1 h/air)	25.3

**Table S2.** Comparison of the maximal NO<sub>x</sub> conversion (conv.), N<sub>2</sub> selectivity, N<sub>2</sub>O yield (100 °C), and NO<sub>2</sub> yield (300 °C) over the Pt-based H<sub>2</sub>-SCR catalyst reported in previous literatures.

Sample	Feed gas composition; Space velocity	Maximal NO <sub>x</sub> conv.	N <sub>2</sub> selectivity	N <sub>2</sub> O yield at 100 °C	NO <sub>2</sub> yield at 300 °C	Ref.
1wt% Pt/Ti-MCM-41	NO/H <sub>2</sub> /O <sub>2</sub> = 0.1%/0.5%/6.7%, He balance; 80,000 h <sup>-1</sup>	88% 140 °C	79% 140 °C	n/a	n/a	[S1]
0.94wt% Pt/Al-MCM-41	NO/H <sub>2</sub> /O <sub>2</sub> = 0.1%/0.5%/6.7%, He balance; 80,000 h <sup>-1</sup>	80% 120 °C	85% 120 °C	n/a	n/a	[S2]
1wt% Pt/ZSM-35	NO/H <sub>2</sub> /O <sub>2</sub> = 0.1%/0.5%/6.7%, He balance; 80,000 h <sup>-1</sup>	81% 120 °C	69% 120 °C	n/a	n/a	[S3]
0.5wt% Pt/H-FER	NO/NO <sub>2</sub> /H <sub>2</sub> /O <sub>2</sub> = 0.091%/0.009%/0.5%/10%, He balance; 36,000 h <sup>-1</sup>	87% 110 °C	69% 110 °C	n/a	54%	[S4]
0.5wt% Pt/HY	NO/H <sub>2</sub> /O <sub>2</sub> = 0.1%/0.5%/10%, He balance; 32,000 h <sup>-1</sup>	81% 130 °C	75% 130 °C	n/a	n/a	[S5]
1wt% Pt/SSZ-13	NO/H <sub>2</sub> /H <sub>2</sub> O/O <sub>2</sub> = 0.1%/0.5%/5%/10%, He balance; 20,000 h <sup>-1</sup>	98% 100 °C	23% 100 °C	80%	60%	[S6]
1.5wt% Pt/ZSM-5	NO/H <sub>2</sub> /H <sub>2</sub> O/O <sub>2</sub> = 0.05%/0.5%/5%/5%, He balance; 120,000 ml/h · g <sub>cat</sub>	99% 75 °C	79% 75 °C	n/a	22%	[S7]
2wt% Pt/MnO <sub>x</sub>	NO/H <sub>2</sub> /O <sub>2</sub> = 0.048%/0.8%/5%, He balance; 78,000 h <sup>-1</sup>	63% 100 °C	30% 100 °C	34%	n/a	[S8]
1wt% Pt/Ti <sub>0.5</sub> Zr <sub>0.5</sub> (TiO <sub>2</sub> +ZrO <sub>2</sub> +ZrTiO <sub>4</sub> )	NO/H <sub>2</sub> /O <sub>2</sub> = 0.03%/0.24%/5%, N <sub>2</sub> balance; 36,000 h <sup>-1</sup>	97% 130 °C	60% 130 °C	n/a	13% (250 °C)	[S9]
0.49wt% Pt (ads.)/ZrP nanosheet	NO/H <sub>2</sub> /O <sub>2</sub> = 0.02%/0.5%/10%, He balance; 120,000 ml/h · g <sub>cat</sub> , ~50,000 h <sup>-1</sup>	89% 150 °C	83% 150 °C	16%	9%	This work

**Table S3.** Percentages of Pt species of 0.08-0.49 wt% Pt (ads.)/ZrP nanosheet and 0.16 wt% Pt (imp.)/ZrP nanosheet (XPS analysis).

Pt loading amount of Pt/ZrP nanosheet / wt%	Method	Pt <sup>0</sup> / %	Pt <sup>II</sup> -O / %	Pt <sup>IV</sup> -O / %
0.08	Ads.	33.4	47.8	18.8
0.14	Ads.	31.4	48.9	19.7
0.22	Ads.	29.3	56.5	14.2
0.49	Ads.	29.2	58.3	12.5
0.16	Imp.	30.4	56.2	13.4

**Table S4.** Percentages of Pt species of 0.4 wt% Pt (ads.)/ZrP<sub>2</sub>O<sub>7</sub> and 0.5 wt% Pt (ads.)/ $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (XPS analysis).

Samples	Method	Pt <sup>0</sup> / %	Pt <sup>II</sup> -O / %	Pt <sup>IV</sup> -O / %
0.4 wt% Pt/ZrP <sub>2</sub> O <sub>7</sub>	Ads.	54.1	32.7	13.2
0.5 wt% Pt/ $\alpha$ -Zr(HPO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Ads.	34.4	49.0	16.6

## References

- [S1] L. Li, P. Wu, Q. Yu, G. Wu, N. Guan, *Appl. Catal. B*, 2010, *94*, 254-262.
- [S2] P. Wu, L. Li, Q. Yu, G. Wu, N. Guan, *Catal. Today*, 2010, *158*, 228-234.
- [S3] Q. Yu, M. Richter, F. Kong, L. Li, G. Wu, N. Guan, *Catal. Today*, 2010, *158*, 452-458.
- [S4] S. Yang, X. Wang, W. Chu, Z. Song, S. Zhao, *Appl. Catal. B*, 2011, *107*, 380-385.
- [S5] X. Zhang, X. Wang, X. Zhao, Y. Xu, H. Gao, F. Zhang, *Chem. Eng. J.*, 2014, *252*, 288-297.
- [S6] J. Shao, P. H. Ho, D. Creaser, L. Olsson, *Appl. Catal. O*, 2024, *188*, 206947.
- [S7] D. C. Park, S. Moon, J. H. Song, H. Kim, E. Lee, Y. H. Lim, D. H. Kim, *Catal. Today*, 2024, *425*, 114318.
- [S8] S. M. Park, M. -Y. Kim, E. S. Kim, H. -S. Han, G. Seo, *Appl. Catal. A*, 2011, *395*, 120-128.
- [S9] Y. Li, D. He, H. Zhao, M. Pei, Y. Fan, H. Xu, J. Wang, Y. Chen, *Chem. Eng. J.*, 2024, *490*, 151714.