

Supporting Information

Facile synthesis of a molybdenum phosphide (MoP) nanocomposite Pt support for high performance methanol oxidation

Jinliang Zhu,^{*a} Shangli Huang,^a Julian Key,^a Shuangxi Nie,^b Shaojian Ma^{*a} and Pei Kang Shen^{*a}

^a Collaborative Innovation Center of Renewable Energy Materials, Guangxi Key Laboratory of Electrochemical Energy Materials, School of Chemistry and Chemical Engineering, Guangxi University, Nanning, 530004, PR China.

^b Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, Nanning 530004, PR China.

* Corresponding authors. Tel.: +86 07713237990; jlzhu85@163.com (Jinliang Zhu); msj3503@sina.com (Shaojian Ma); stsspk@mail.sysu.edu.cn (Pei Kang Shen).

Table S1. The synthesis methods of molybdenum phosphide reported in literatures

Molybdenum phosphide	Morphology	Synthesis	Phosphorus source and precursor	Ref.
MoP	Micro particle	Solid state synthesis	Red phosphorus + Mo	[1]
MoP	Micro powder	Solid state synthesis	LiO ₃ P + Mo	[2]
MoP	Particle	Solid state synthesis	Na ₃ P ₃ O ₉ + Mo	[3]
MoP	Particle	Solid state synthesis (in H ₂)	(NH ₄) ₂ HPO ₄ (or NaH ₂ PO ₂) + MoO ₃	[4, 5]
MoP	Bulk	Hydrothermal synthesis	(NH ₄) ₂ HPO ₄ + (NH ₄) ₆ Mo ₇ O ₂₄ ·xH ₂ O	[6-8]
MoP	Bulk	Calcination in air + reduction in H ₂	(NH ₄) ₂ HPO ₄ + (NH ₄) ₆ Mo ₇ O ₂₄ •4H ₂ O	[9-14]
MoP	Bulk	Solid state synthesis (in H ₂)	P ₂ O ₅ + (NH ₄) ₆ Mo ₇ O ₂₄ •4H ₂ O	[15]
MoP	Bulk	Sintered + reduced in H ₂	(NH ₄) ₂ HPO ₄ + (NH ₄) ₆ Mo ₇ O ₂₄ •4H ₂ O	[16]
MoP	Particle	Hydrothermal synthesis + reduction in dimethyl ether	(NH ₄) ₂ HPO ₄ + (NH ₄) ₆ Mo ₇ O ₂₄ •4H ₂ O	[17]
MoP	Particle	Thermal reduction by hydrogen plasma	P ₂ O ₅ + MoO ₃	[18, 19]
MoP	Nanoparticle	Calcination in air + reduction in H ₂	(NH ₄) ₂ HPO ₄ + synthesized MoO ₂ nanoparticles	[20]
MoP NA/CC	Sheet	Solid state synthesis	Red phosphorus + synthesized MoS ₂ NA/CC	[21]
MoP	Bulk	Solid state synthesis (in H ₂)	NH ₄ H ₂ PO ₄ + (NH ₄) ₆ Mo ₇ O ₂₄ •4H ₂ O	[22]
MoP /SN	Particle	Hydrothermal synthesis + calcination in H ₂	H ₃ PO ₄ +H ₃ PMo ₁₂ O ₄₀ •nH ₂ O + (thio)urea	[23]
MoP	Single crystal bulk	Solid-state reaction (Ge as the flux)	P + Mo	[24]

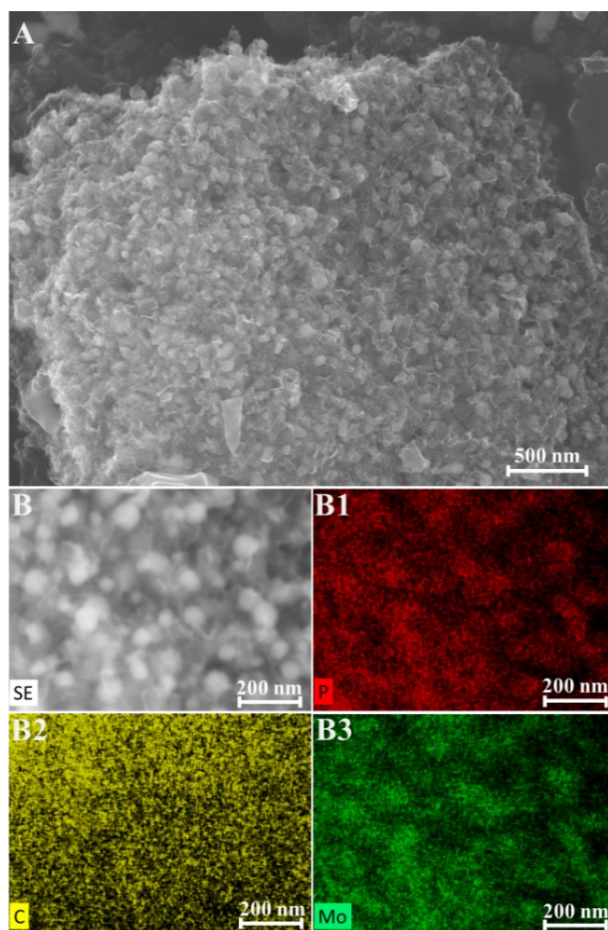


Fig. S1 (A, B) SEM images of the MoP/C⁽²⁾ and (B1-B3: P, C and Mo respectively) element mappings of the MoP/C⁽²⁾.

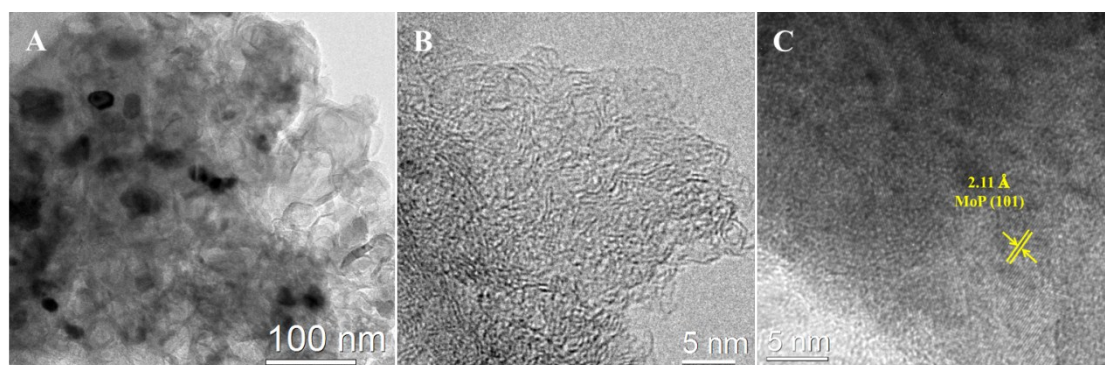


Fig. S2 TEM and HRTEM images of MoP/C⁽²⁾

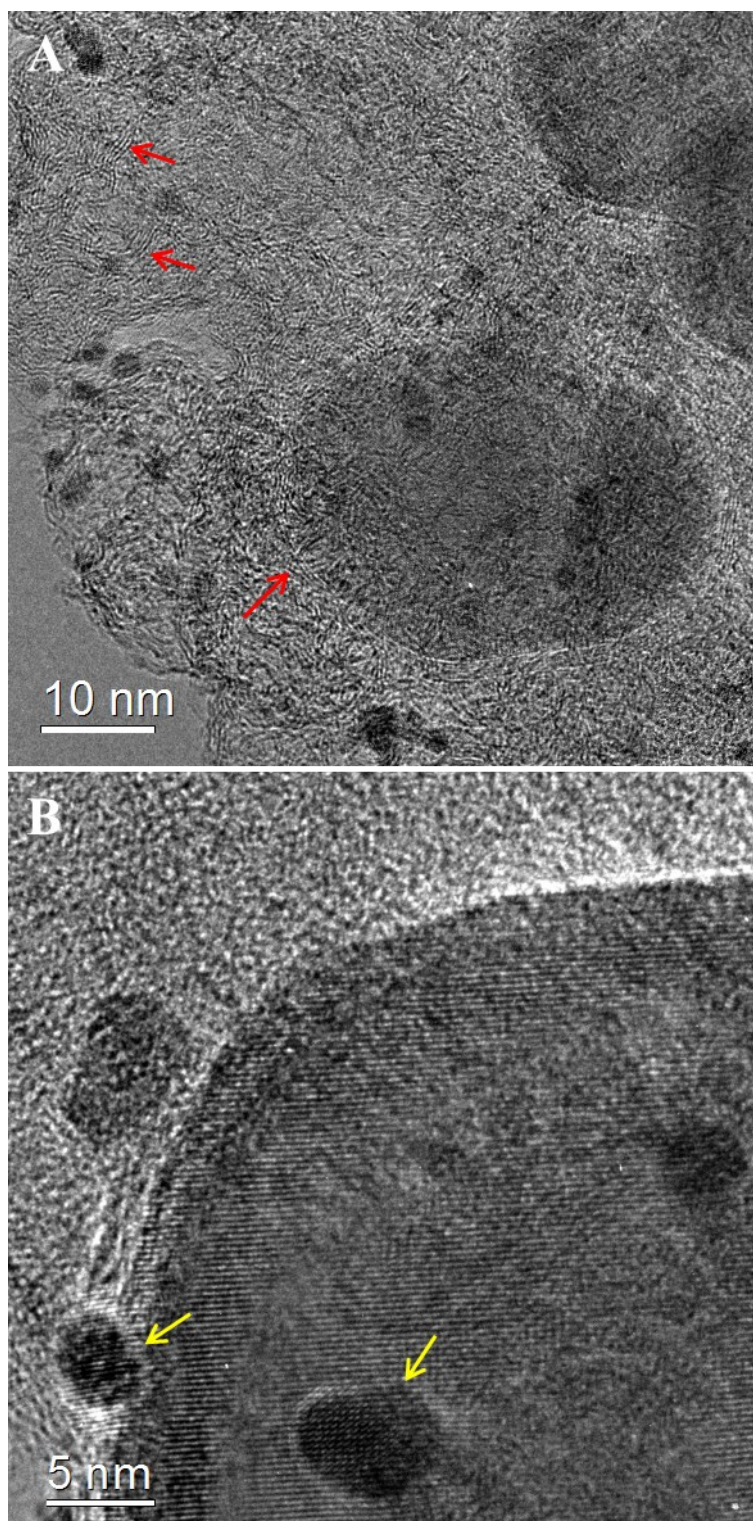


Fig. S3 Enlarged TEM images of Pt-MoP/C⁽²⁾

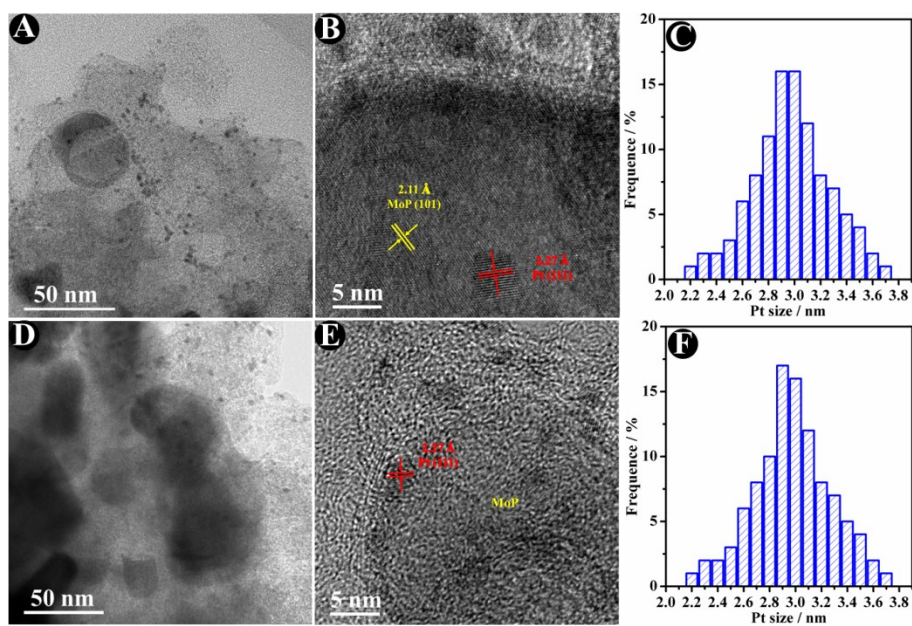


Fig. S4 TEM and HRTEM images of (A, B) Pt-MoP/C⁽¹⁾ and (D, E) Pt-MoP/C⁽³⁾, size-distribution histogram of Pt nanoparticles on: (C) Pt-MoP/C⁽¹⁾ and (F) Pt-MoP/C⁽³⁾.

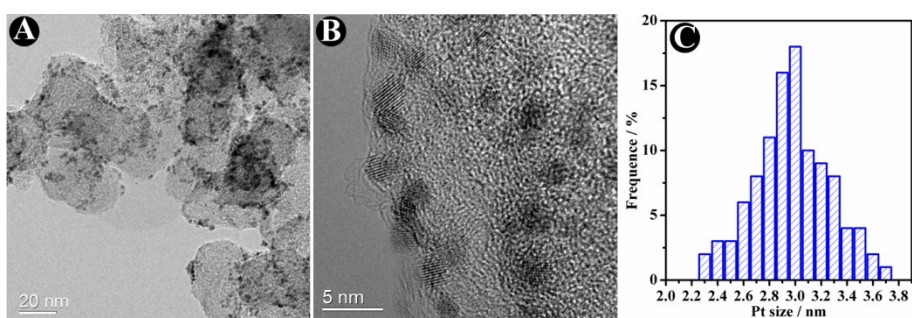


Fig. S5 TEM (A) and HRTEM (B) images of Pt/C_{free} and size-distribution histogram (C) of Pt nanoparticles on Pt/C_{free}.

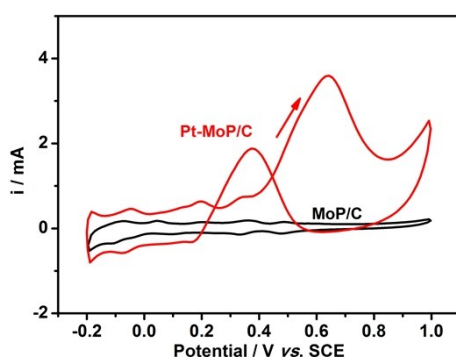


Fig. S6 CVs of MoP/C and Pt-MoP/C⁽¹⁾ in 0.5 M H₂SO₄ + 1.0 M CH₃OH solution at 50 mV s⁻¹.

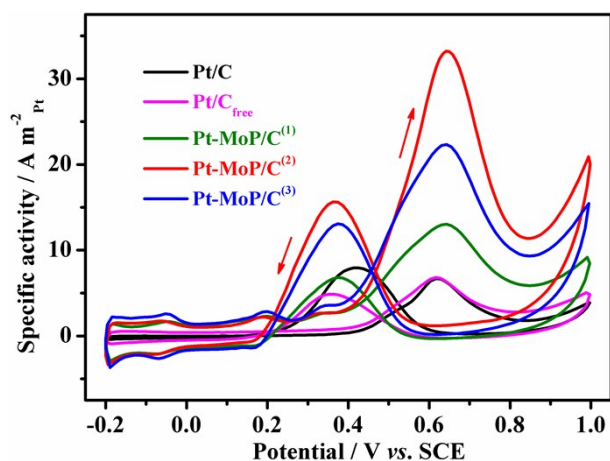


Fig. S7 Specific activity of commercial Pt/C, Pt/C_{free} and Pt-MoP/C catalysts illustrated by their cyclic voltammograms in 0.5 M H₂SO₄ + 1.0 M CH₃OH solution at 50 mV s⁻¹.

Table S2. Electrocatalytically active surface areas (ECSAs) estimated from hydrogen absorption and specific activity of the catalysts

Samples	ECSAs (m ² g ⁻¹)	Specific activity
		(A m ⁻²)
Pt-MoP/C ⁽¹⁾	55.21	13.04
Pt-MoP/C ⁽²⁾	56.01	32.94
Pt-MoP/C ⁽³⁾	55.58	22.33
Pt/C _{free}	54.87	6.79
Pt/C	54.69	6.69

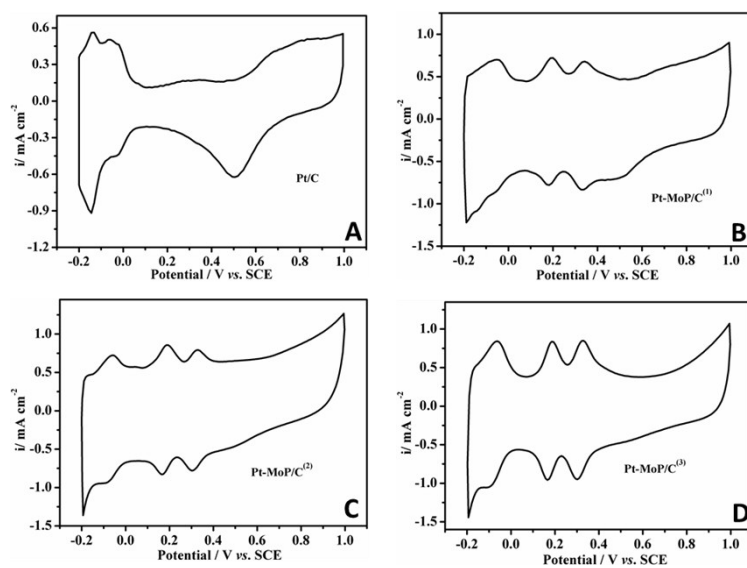


Fig. S8 CVs of commercial Pt/C and Pt-MoP/C catalysts in 0.5 M H₂SO₄ at 50 mV s⁻¹.

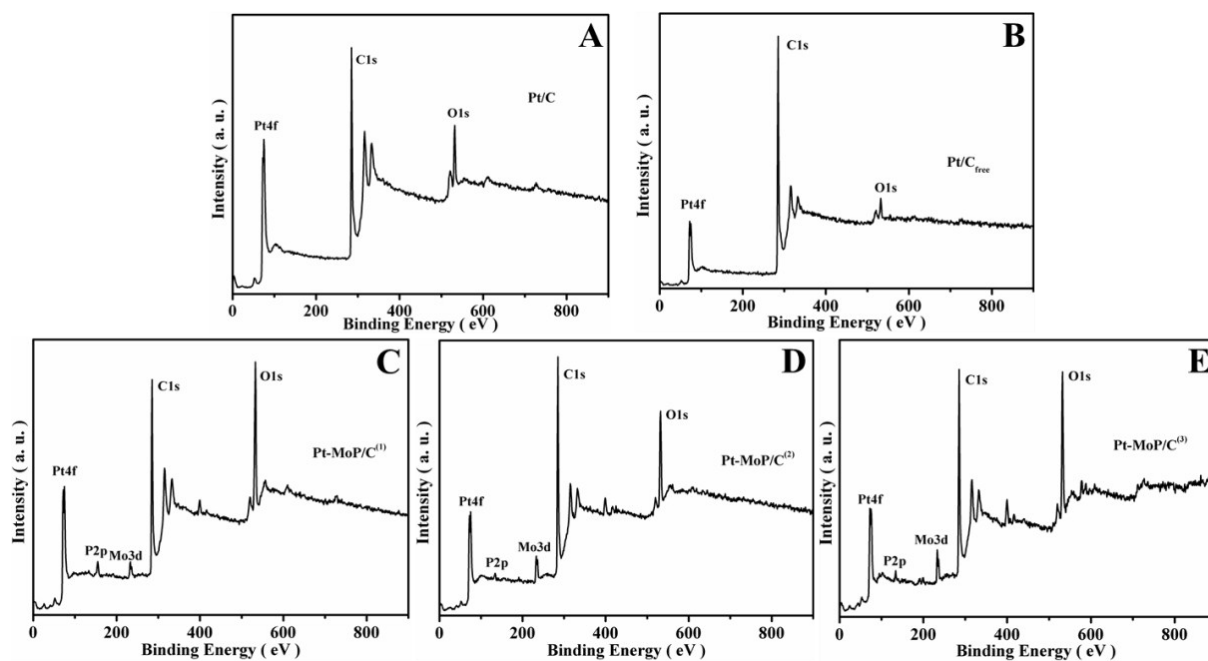


Fig. S9 XPS spectra of the Pt/C, Pt/C_{free} and Pt-MoP/C catalysts.

Table S3. XPS analysis of the samples (surface atomic ratios of the samples)

Samples	Carbon (at.%)	Phosphorus (at.%)	Molybdenum (at.%)	Platinum (at.%)
Pt-MoP/C ⁽¹⁾	66.48	1.78	1.24	2.83
Pt-MoP/C ⁽²⁾	74.39	1.84	1.35	2.24
Pt-MoP/C ⁽³⁾	74.91	2.31	1.77	1.47
Pt/C _{free}	74.73	0.74	---	1.48
Pt/C	81.49	---	---	5.51

Table S4. Electrochemical Parameters of methanol electrooxidation catalysts

Catalysts	Potential shift [†]	I_f/I_b	Activity ratio [‡]	Test conditions
PtNi/CNT ^[25]	---	1.1	1.4	1 M CH ₃ OH/0.5 M H ₂ SO ₄
Pt ₃ V/C ^[26]	-100 mV	--	---	0.1 M HClO ₄ +1 M CH ₃ OH
Nanoporous Pt–Cu microwires ^[27]	---	1.58	1.6	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH
Pd–Pt alloy ^[28]	---	1.60	2.0	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH
Pt/S-RGO ^[29]	---	1.36	1.8	0.5 M H ₂ SO ₄ +2.0 M CH ₃ OH
Pt-Co ₂ P/C ^[30]	-120 mV	1.19	---	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH
Pt/Ti _{0.7} Ru _{0.3} O ₂ ^[31]	-100 mV	---	---	0.1 M H ₂ SO ₄ +0.5 M CH ₃ OH
Pt/Ru ^[31]	-100 mV	---	---	
np-PtCuTi ^[32]	quite similar	1.36	4.2	0.5 M H ₂ SO ₄ +0.5 M CH ₃ OH
Ru@Pt ^[33]	-120 mV	---	2.72	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH
Pt _{3.5} Pb NNWs ^[34]	---	1.18	3.45	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH
Pt/NOMC-3D ^[35]	-50 mV	1.1	1.22	0.5 M CH ₃ OH+0.1 M HClO ₄
PtZn/MWNT-E ^[36]	---	1.46	1.4	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH
This work (Pt-MoP/C)	-140 mV	2.1	5.1	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH

Potential shift[†] is the onset peak potential shift of a catalyst compared with that of Pt/C in CH₃OH oxidation.

Activity ratio[‡] is the peak mass activity ratio of a catalyst to that of Pt/C.

I_f/I_b is the ratio of the forward peak current density (I_f) to the backward peak current density (I_b).

--- denotes no data mentioned in the references.

Compared with the latest reported Pt-based catalysts^[25-30, 32-36], the Pt-MoP/C in this work shows the biggest I_f/I_b and peak mass activity ratio. The onset peak potential of Pt-MoP/C toward methanol oxidation is 140 mV more negative than that of Pt/C, which is also superior to that of reported Pt/Ti_{0.7}Ru_{0.3}O₂^[31], Ru@Pt^[33] and the state-of-the-art catalyst (Pt/Ru)^[31].

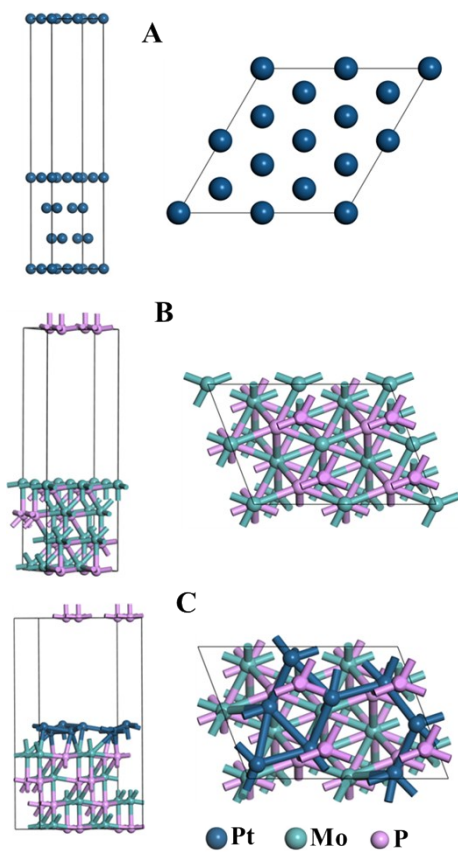


Fig. S10 Side and top views of (A) Pt(111), (b) MoP(101) and (c) Pt(111)_{1ML}-MoP(101).

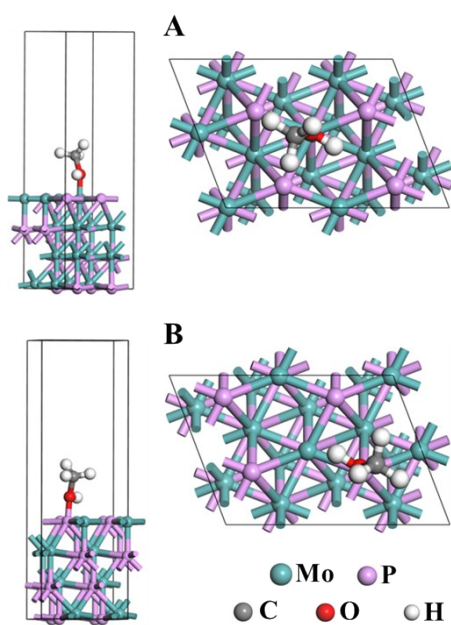


Fig. S11 Side and top views of (A) MoP(101)-CH₃OH-T1 and (B) MoP(101)-CH₃OH-T2.

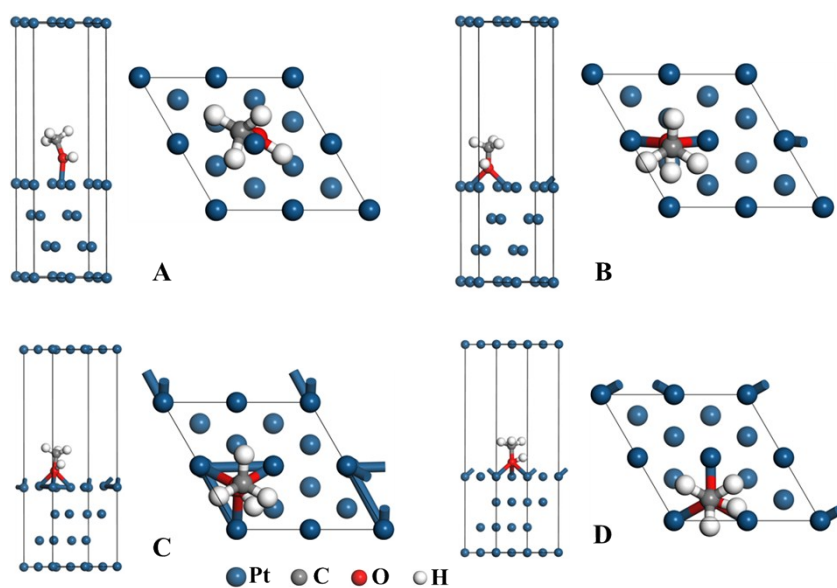


Fig. S12 Side and top views of (A) Pt(111)-CH₃OH-T, (B) Pt(111)-CH₃OH-B, (C) Pt(111)-CH₃OH-H and (d) Pt(111)-CH₃OH-F.

Table S5. Computed adsorption energies (E_{ads} , eV) per molecule and structural parameters (d , Å) of methanol on MoP(101), Pt(111) and Pt(111)_{IML}-MoP(101)

	E_{ads}	$d(\text{O-Mo})$	$d(\text{O-P})$	$d(\text{O-Pt})$	$d(\text{C-O})$	$d(\text{H-O})$
MoP(101)-T1	-0.651	2.308			1.447	0.976
MoP(101)-T2	-0.651		3.516		1.430	0.979
Pt(111)-T	-0.186			2.308	1.510	1.110
Pt(111)-B	-0.079			3.158, 3.233	1.431	0.978
Pt(111)-H	-0.151			3.202, 3.559, 4.001	1.430	0.981
Pt(111)-F	-0.150			3.190, 3.206, 3.526	1.431	0.978
Pt(111) _{IML} -MoP(101)	-0.267			2.574	1.442	0.978

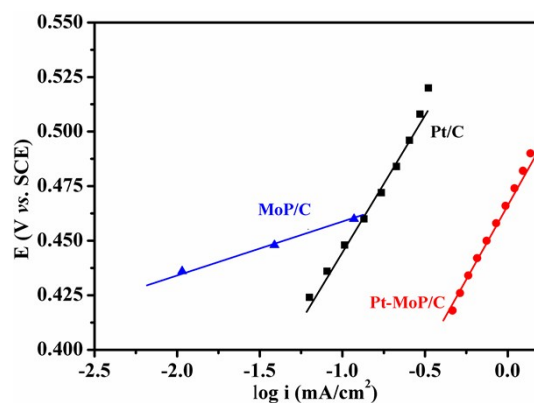


Fig. S13 Tafel plots for the MoP/C, Pt/C and Pt-MoP/C⁽²⁾ catalysts in 0.5 M H₂SO₄ + 1.0 M CH₃OH solution at 5 mV s⁻¹.

References

- [1] F. E. Faller and W. Biltz, *Zeitschrift für anorganische und allgemeine Chemie*, 1941, **248**, 209-228.
- [2] V. V. Lesnyak, D. A. Stratiichuk, V. S. Sudavtsova and M. S. Slobodyanik, *Russian Journal of Applied Chemistry*, 2001, **74**, 1274-1277.
- [3] A. B. Aueshov, L. V. Levchenko, S. Z. Eskibaeva, E. S. Shustikova and V. A. Sinyaev, *Inorganic Materials*, 2000, **36**, 935-937.
- [4] Z. Yao, Z. Lai, X. Zhang, F. Peng, H. Yu and H. Wang, *Materials Research Bulletin*, 2011, **46**, 1938-1941.
- [5] Q. Guan and W. Li, *Journal of Catalysis*, 2010, **271**, 413-415.
- [6] J. Bai, X. Li, A. Wang, R. Prins and Y. Wang, *Journal of Catalysis*, 2012, **287**, 161-169.
- [7] Z. W. Yao, L. Wang and H. Dong, *J Alloy Compd*, 2009, **473**, L10-L12.
- [8] P. A. Clark and S. T. Oyama, *Journal of Catalysis*, 2003, **218**, 78-87.
- [9] R. Cheng, Y. Shu, M. Zheng, L. Li, J. Sun, X. Wang and T. Zhang, *Journal of Catalysis*, 2007, **249**, 397-400.
- [10] C. Stinner, R. Prins and T. Weber, *Journal of Catalysis*, 2000, **191**, 438-444.
- [11] Z. Wu, F. Sun, W. Wu, Z. Feng, C. Liang, Z. Wei and C. Li, *Journal of Catalysis*, 2004, **222**, 41-52.
- [12] Z. Xing, Q. Liu, A. M. Asiri and X. Sun, *Advanced materials*, 2014, **26**, 5702-5707.
- [13] Y. Duan, Y. Sun, L. Wang, Y. Dai, B. Chen, S. Pan and J. Zou, *Journal of Materials Chemistry A*, 2016, **4**, 7674-7682.
- [14] Z. Yao, Y. Su, C. Lu, C. Yang, Z. Xu, J. Zhu, X. Zhuang and F. Zhang, *New Journal of Chemistry*, 2016, **40**, 6015-6021.
- [15] L. Guo, Y. Zhao and Z. Yao, *Dalton T*, 2016, **45**, 1225-1232.

- [16] C. Deng, F. Ding, X. Li, Y. Guo, W. Ni, H. Yan, K. Sun and Y.-M. Yan, *Journal of Materials Chemistry A*, 2016, **4**, 59-66.
- [17] Z. Yao, M. Li, X. Wang, X. Qiao, J. Zhu, Y. Zhao, G. Wang, J. Yin and H. Wang, *Dalton T*, 2015, **44**, 5503-5509.
- [18] J. Guan, Y. Wang, M. Qin, Y. Yang, X. Li and A. Wang, *Journal of Solid State Chemistry*, 2009, **182**, 1550-1555.
- [19] A. Wang, M. Qin, J. Guan, L. Wang, H. Guo, X. Li, Y. Wang, R. Prins and Y. Hu, *Angewandte Chemie International Edition*, 2008, **47**, 6052-6054.
- [20] J. Yang, F. Zhang, X. Wang, D. He, G. Wu, Q. Yang, X. Hong, Y. Wu and Y. Li, *Angewandte Chemie*, 2016, **128**, 13046-13050.
- [21] Z. Pu, S. Wei, Z. Chen and S. Mu, *Applied Catalysis B: Environmental*, 2016, **196**, 193-198.
- [22] S.-L. Fang, T.-C. Chou, S. Samireddi, K.-H. Chen, L.-C. Chen and W.-F. Chen, *Open Science*, 2017, **4**, 161016.
- [23] M. A. R. Anjum and J. S. Lee, *ACS Catalysis*, 2017, **7**, 3030-3038.
- [24] B. Lv, Z.-L. Feng, Q.-N. Xu, X. Gao, J.-Z. Ma, L.-Y. Kong, P. Richard, Y.-B. Huang, V. Strocov and C. Fang, *Nature*, 2017, **546**, 627-631.
- [25] A. B. A. A. Nassr, I. Sinev, M.-M. Pohl, W. Grünert and M. Bron, *Acs Catal*, 2014, **4**, 2449-2462.
- [26] Z. Cui, H. Chen, M. Zhao, D. Marshall, Y. Yu, H. Abruña and F. J. DiSalvo, *J Am Chem Soc*, 2014, **136**, 10206-10209.
- [27] H.-J. Qiu, X. Shen, J. Wang, A. Hirata, T. Fujita, Y. Wang and M. Chen, *Acs Catal*, 2015, **5**, 3779-3785.
- [28] G. Zhang, C. Huang, R. Qin, Z. Shao, D. An, W. Zhang and Y. Wang, *J Mater Chem A*, 2015, **3**, 5204-5211.
- [29] Y. Noh, Y. Kim, S. Lee, E. J. Lim, J. G. Kim, S. M. Choi, M. H. Seo and W. B. Kim, *Nanoscale*, 2015, **7**, 9438-9442.
- [30] J. Zhu, G. He and P. K. Shen, *J Power Sources*, 2015, **275**, 279-283.
- [31] M. Obradović, U. Lačnjevac, B. Babić, P. Ercius, V. Radmilović, N. Krstajić and S. L. Gojković, *Applied Catalysis B: Environmental*, 2015, **170**, 144-152.
- [32] Y. Wang, K. Yin, J. Zhang, C. Si, X. Chen, L. Lv, W. Ma, H. Gao and Z. Zhang, *Journal of Materials Chemistry A*, 2016, **4**, 14657-14668.
- [33] J. Xie, Q. Zhang, L. Gu, S. Xu, P. Wang, J. Liu, Y. Ding, Y. F. Yao, C. Nan and M. Zhao, *Nano Energy*, 2016, **21**, 247-257.
- [34] L. Huang, Y. Han, X. Zhang, Y. Fang and S. Dong, *Nanoscale*, 2017, **9**, 201-207.
- [35] G.-f. Long, X.-h. Li, K. Wan, Z.-x. Liang, J.-h. Piao and P. Tsiakaras, *Applied Catalysis B: Environmental*, 2017, **203**, 541-548.
- [36] Z. Qi, C. Xiao, C. Liu, T. W. Goh, L. Zhou, R. Maligal-Ganesh, Y. Pei, X. Li, L. A. Curtiss and W. Huang, *Journal of the American Chemical Society*, 2017, **139**, 4762-4768.