Article

Reactive metal–support interactions at moderate temperature in two-dimensional niobium-carbide-supported platinum catalysts

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Abstract

The reactive metal–support interaction (RMSI) offers electronic, geometric and compositional effects that can be used to tune catalytic active sites. Generally, supports other than oxides are disregarded as candidates for RMSI. Here, we report an example of non-oxide-based RMSI between platinum and Nb_2CT_x MXene—a recently developed, two-dimensional metal carbide. The surface functional groups of the two-dimensional carbide can be reduced, and a Pt–Nb surface alloy is formed at a moderate temperature (350 °C). Such an alloy exhibits weaker CO adsorption than monometallic platinum. Water-gas shift reaction kinetics reveals that the RMSI stabilizes the nanoparticles and creates alloy–MXene interfaces with higher H_2O activation ability compared with a non-reducible support or a bulk niobium carbide. This RMSI between platinum and the niobium MXene support can be extended to other members of the MXene family and opens new avenues for the facile design and manipulation of functional bimetallic catalysts.

Additional information

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References

1. Yu, W., Porosoff, M. D. & Chen, J. G. Review of Pt-based bimetallic catalysis: from model surfaces to supported catalysts. *Chem. Rev.* **112**, 5780–5817 (2012).

2. Sankar, M. et al. Designing bimetallic catalysts for a green and sustainable future. *Chem. Soc. Rev.* **41**, 8099–8139 (2012).

3. Wang, H., Wang, C., Yan, H., Yi, H. & Lu, J. Precisely-controlled synthesis of Au@Pd core–shell bimetallic catalyst via atomic layer deposition for selective oxidation of benzyl alcohol. *J. Catal.* **324**, 59–68 (2015).

4. Armbrüster, M. *Intermetallic Compounds in Catalysis*, *Encyclopedia of Catalysis* (Wiley, Weinheim, 2011).

5. Penner, S. & Armbrüster, M. Formation of intermetallic compounds by reactive metal–support interaction: a frequently encountered phenomenon in catalysis. *ChemCatChem* **7**, 374–392 (2015).

6. Wang, D. et al. Silicide formation on a Pt/SiO_2 model catalyst studied by TEM, EELS, and EDXS. *J. Catal.* **219**, 434–441 (2003).

7. Penner, S. et al. Platinum nanocrystals supported by silica, alumina and ceria: metal–support interaction due to high-temperature reduction in hydrogen. *Surf. Sci.* **532**, 276–280 (2003).

8. Lukatskaya, M. R. et al. Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. *Science* **341**, 1502–1505 (2013).

9. Naguib, M., Mochalin, V. N., Barsoum, M. W. & Gogotsi, Y. 25th anniversary article: MXenes: a new family of two-dimensional materials. *Adv. Mater.* **26**, 992–1005 (2014).

10. Anasori, B., Lukatskaya, M. R. & Gogotsi, Y. 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* **2**, 16098 (2017).

11. Ma, T. Y., Cao, J. L., Jaroniec, M. & Qiao, S. Z. Interacting carbon nitride and titanium carbide nanosheets for high-performance oxygen evolution. *Angew. Chem. Int. Ed.* **55**, 1138–1142 (2016).

12. Ran, J. et al. Ti_3C_2 MXene co-catalyst on metal sulfide photo-absorbers for enhanced visible-light photocatalytic hydrogen production. *Nat. Commun.* **8**, 13907 (2017).

13. Schreier, M. & Regalbuto, J. R. A fundamental study of Pt tetraammine impregnation of silica: 1. The electrostatic nature of platinum adsorption. *J. Catal.* **225**, 190–202 (2004).

14. Lambert, S. et al. Synthesis of very highly dispersed platinum catalysts supported on carbon xerogels by the strong electrostatic adsorption method. *J. Catal.* **261**, 23–33 (2009).

15. Lu, J., Zhang, X., Bravo-Suarez, J. J., Fujitani, T. & Oyama, S. T. Effect of composition and promoters in Au/TS-1 catalysts for direct propylene epoxidation using H_2 and O_2. *Catal. Today* **147**, 186–195 (2009).

16. Rakhi, R., Ahmed, B., Hedhili, M. N., Anjum, D. H. & Alshareef, H. N. Effect of postetch annealing gas composition on the structural and electrochemical properties of Ti_2CT_x MXene electrodes for supercapacitor applications. *Chem. Mater.* **27**, 5314–5323 (2015).

17. Naguib, M. et al. New two-dimensional niobium and vanadium carbides as promising materials for Li-ion batteries. *J. Am. Chem. Soc.* **135**, 15966–15969 (2013).

18. Sabnis, K. D. et al. Water-gas shift catalysis over transition metals supported on molybdenum carbide. *J. Catal.* **331**, 162–171 (2015).

19. Shekhar, M. *Water-Gas Shift Catalysis Over Supported Gold and Platinum Nanoparticles* PhD thesis, Purdue Univ. (2012).

20. Sabnis, K. D. et al. Probing the active sites for water-gas shift over Pt/molybdenum carbide using multi-walled carbon nanotubes. *J. Catal.* **330**, 442–451 (2015).

21. Balakrishnan, K. & Schwank, J. A chemisorption and XPS study of bimetallic Pt–Sn/Al_2O_3 catalysts. *J. Catal.* **127**, 287–306 (1991).

22. Wakisaka, M. et al. Electronic structures of Pt–Co and Pt–Ru alloys for CO-tolerant anode catalysts in polymer electrolyte fuel cells studied by EC-XPS. *J. Phys. Chem. B* **110**, 23489–23496 (2006).

23. Beard, B. C. & Ross, P. N. Platinum–titanium alloy formation from high-temperature reduction of a titania-impregnated platinum catalyst: implications for strong metal–support interaction. *J. Phys. Chem.* **90**, 6811–6817 (1986).

24. Hammer, B., Morikawa, Y. & Nørskov, J. K. CO chemisorption at metal surfaces and overlayers. *Phys. Rev. Lett.* **76**, 2141–2144 (1996).

25. Gauthier, Y. et al. Adsorption sites and ligand effect for CO on an alloy surface: a direct view. *Phys. Rev. Lett.* **87**, 036103 (2001).

26. Schaidle, J. A., Schweitzer, N. M., Ajenifujah, O. T. & Thompson, L. T. On the preparation of molybdenum carbide-supported metal catalysts. *J. Catal.* **289**, 210–217 (2012).

27. Cui, Y. et al. Participation of interfacial hydroxyl groups in the water-gas shift reaction over Au/MgO catalysts. *Catal. Sci. Technol.* **7**, 5257–5266 (2017).

28. Hu, C. et al. In situ reaction synthesis, electrical and thermal, and mechanical properties of Nb_4AlC_3. *J. Am. Ceram. Soc.* **91**, 2258–2263 (2008).

29. Wang, X. & Zhou, Y. Microstructure and properties of Ti_3AlC_2 prepared by the solid–liquid reaction synthesis and simultaneous in-situ hot pressing process. *Acta Mater.* **50**, 3143–3151 (2002).

30. Bollmann, L. et al. Effect of Zn addition on the water-gas shift reaction over supported palladium catalysts. *J. Catal.* **257**, 43–54 (2008).

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Contributions

Z.L. conceived the research and performed the synthesis and material characterizations. Y.C. and F.H.R. carried out the CO chemisorption and WGS kinetics measurements. Z.W. and J.T.M. carried out the XAS measurements. L.Z., G.M., B.X. and E.S. conducted microscopy analyses. C.M. performed the XPS experiments. Y.W. supervised and led the project.

Competing interests

The authors have filed a patent application (US Patent application no. 62/579,364).

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Supplementary information

Supplementary Information - *https://static-content.springer.com/esm/art%3A10.1038%2Fs41929-018-0067-8/MediaObjects/41929_2018_67_MOESM1_ESM.pdf*

Supplementary Methods; Supplementary Figures 1–13; Supplementary Table 1; Supplementary References

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