Supplementary Material

Computation-Predicted, Stable, and Inexpensive Single-atom Nanocatalyst Pt@Mo_2C–an Important Advanced Material for H_2 Production

Qiaohong Li[1,2,3], Zuju Ma[1], Rongjian Sa[1], Hertanto Adidharma[3], Khaled A. M. Gasem[3], Armistead G Russell[4], Maohong Fan[2, 3, 4*] and Kechen Wu[1*]

[1] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China
[2] School of Energy Resources, University of Wyoming, WY82071, USA
[3]Departments of Chemical & Petroleum Engineering, University of Wyoming, WY82071, USA
[4]School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

[*] Corresponding author. Fax: +1 (307) 7666777.
E-mail address: mfan@uwyo.edu (M. Fan).
[*] Corresponding author. Fax: +86 591 83792932.
E-mail address: wkc@fjirsm.ac.cn (K. Wu).

Table S1 Gibbs free energy for oxidation of Mo_2C[1]

Reaction	Gibbs Free Energy of Reaction (kJ/mol)
$Mo_2C(s) + 4O_2(g) \rightarrow 2MoO_3(s) + CO_2(g)$	-1762
$Mo_2C(s) + 3O_2(g) \rightarrow 2MoO_2(s) + CO_2(g)$	-1394
$Mo_2C(s) + (7/2)O_2(g) \rightarrow 2MoO_3(s) + CO(g)$	-1505
$Mo_2C(s) + (5/2)O_2(g) \rightarrow 2MoO_2(s) + CO(g)$	-1137
$Mo_2C(s) + 8H_2O(l) \rightarrow 2MoO_3(s) + CO_2(g) + 8H_2(g)$	135
$Mo_2C(s) + 6H_2O(l) \rightarrow 2MoO_2(s) + CO_2(g) + 6H_2(g)$	29
$Mo_2C(s) + 7H_2O(l) \rightarrow 2MoO_3(s) + CO(g) + 7H_2(g)$	155
$Mo_2C(s) + 5H_2O(l) \rightarrow 2MoO_2(s) + CO(g) + 5H_2(g)$	49

Two forms of surface oxidations (Figure S1) are provided in. For the first form (a), surface O oxidizes second layers of C atom, leading to generation of CO adsorbed on the C-defect surface. The activation barrier of this step is 2.56 eV with an endothermic energy of 0.95 eV. As to the second kind (b), surface O penetrates into the subsurface. This elementary reaction is endothermic by 3.01 eV with an activation barrier of 3.36 eV. Neither of these two approaches is likely to occur, due to the fact that the corresponding activation barrier of the two forms are higher than that of surface O participating in the WGS reaction.

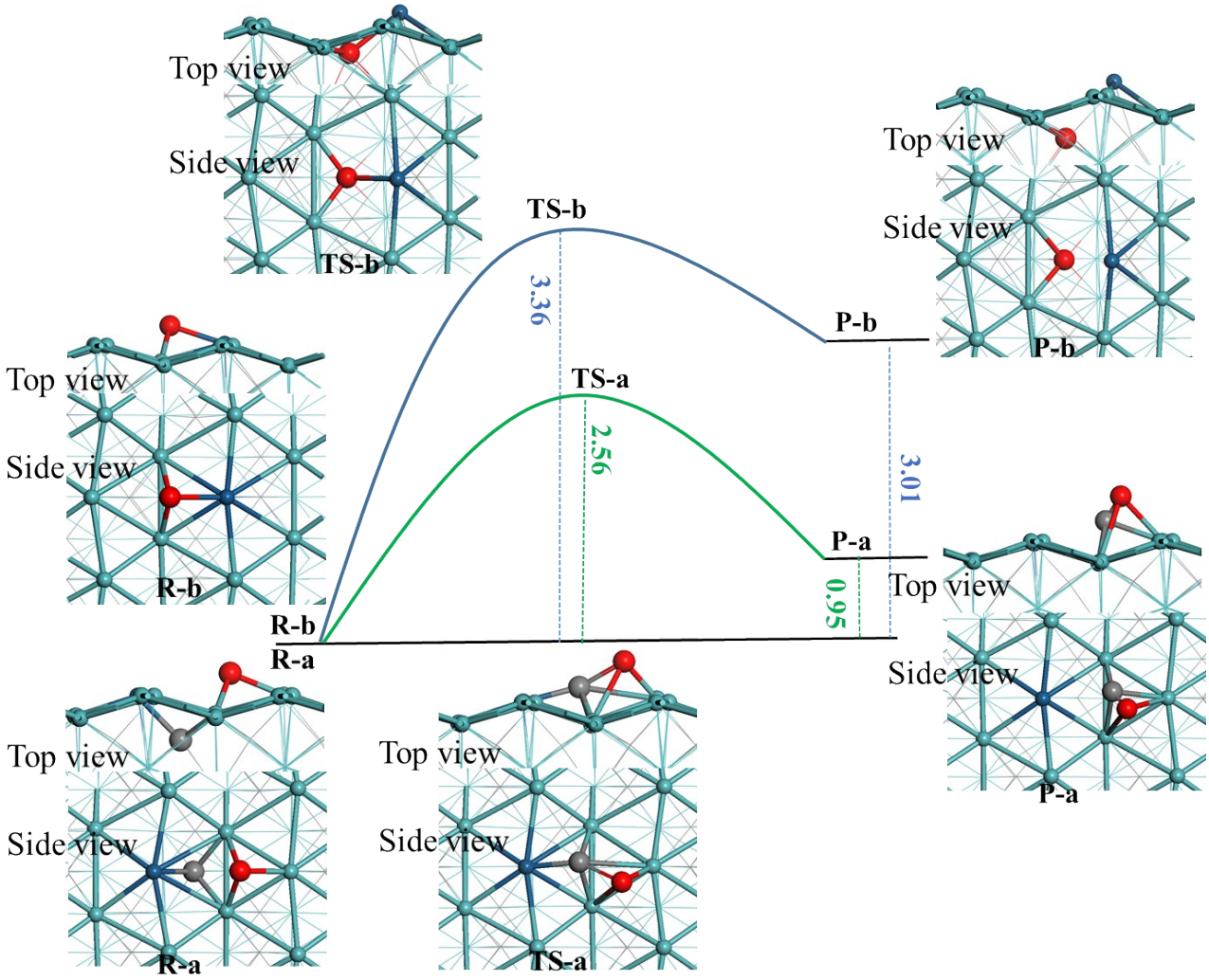

Figure S1 Calculated potential energy diagram for surface oxidation reaction over Pt@α-Mo_2C(001) surface. The energy unit is eV.

References

1. N. M. Schweitzer, J. A. Schaidle, O. K. Ezekoye, X. Pan, S. Linic and L. T. Thompson, *J. Am. Chem. Soc.*, 2011, **133**, 2378-2381.