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Electronic Supporting Information (ESI)

MoS_2 supported platinum single atom and its superior catalytic activity for CO oxidation: a density functional theory study

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S1. Determination of the ground state of the Pt/MoS_2 system

DFT calculations have been used to determine the optimized adsorption configuration of a single platinum atom on the MoS_2 monolayer. In total, four adsorption sites were considered, namely, the BRI site, the HMo site, the TOP site and the HH site (see Fig. S1). The Pt atom at a BRI site is unstable, and moves to the nearest HMo site upon structural relaxation. Based on our calculations, the most stable adsorption site is the HMo site, with an adsorption energy of -2.67eV.

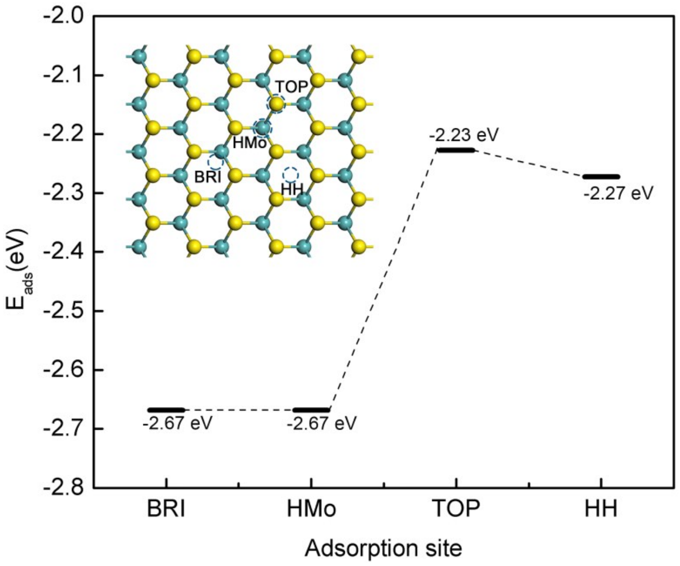

Fig.S1 The optimized adsorption configurations and corresponding adsorption energies of the Pt atom on a MoS_2 monolayer.

S2. The population analysis of the resulting projected states

The Mulliken charge analysis was employed to investigate the charge redistribution of the selected atoms throughout the CO oxidation reaction [1]. Table S1 shows the charge transfer of all adsorbed structures, and the structures involved in the L-H reaction.

Table S1. The Mulliken charge analysis of the selected atoms in the adsorbed configurations and the structures involved in the L-H reaction.

Selected atoms	Adsorption structures				L-H path			
	MoS_2	Pt/MoS_2	CO-Pt/MoS_2	O_2-Pt/MoS_2	IS	TS	MS	FS
Pt atom	0.00	-0.19	0.05	0.14	0.04	0.23	0.17	0.11
S_1 atom	0.03	0.10	-0.12	-0.12	0.05	-	-	0.13
S_2 atom	0.03	0.10	-0.12	-0.11	0.16	0.16	0.25	0.12

S_3 atom	0.03	0.11	-0.12	-0.12	0.03	-	-	0.13
C atom	-	-	0.06	-	0.42	0.44	0.54	0.58
O atom	-	-	-0.11	-	-0.13	-0.11	-0.28	-0.30
CO molecule	-	-	-0.04	-	0.29	0.33	-	-
O_b atom	-	-	-	-0.06	-0.25	-0.42	-0.36	-0.28
O_a atom	-	-	-	-0.09	-0.28	-0.46	-0.48	-0.45
O_aO_b molecule	-	-	-	-0.15	-0.53	-	-	-

S3. The multiple CO and O_2 adsorptions on the Pt/MoS_2 surface

We also investigate the multiple CO molecules and O_2 molecules adsorptions on the Pt/MoS_2 surface respectively to verify the stability of the single Pt atom adsorbed on MoS_2. Here we calculated the adsorption energy of multiple adsorption types of the CO and O_2 adsorption on the Pt/MoS_2 respectively in order to discuss the completion between the adsorption of the second CO molecule with the adsorption of O_2 clearly. The adsorption energy is -2.39 eV, -1.19 eV and -0.95 eV for the first, second and third CO molecule, respectively. In terms of energy, the most stable configuration is one CO molecule adsorbing on each Pt atom, if the CO molecule is more than the Pt atoms, it seems that it is possible that multiple CO molecules adsorb on one Pt atom under these conditions. However, taking into consideration that the working environment of CO oxidation is normally O_2-rich or in the presence of large amounts of H_2, the Pt atom will firstly be occupied by the O_2 molecules and the large free energy change during the reaction process will separate the CO molecules from each other. As a consequence, the multiple adsorption of CO on Pt is unlikely.

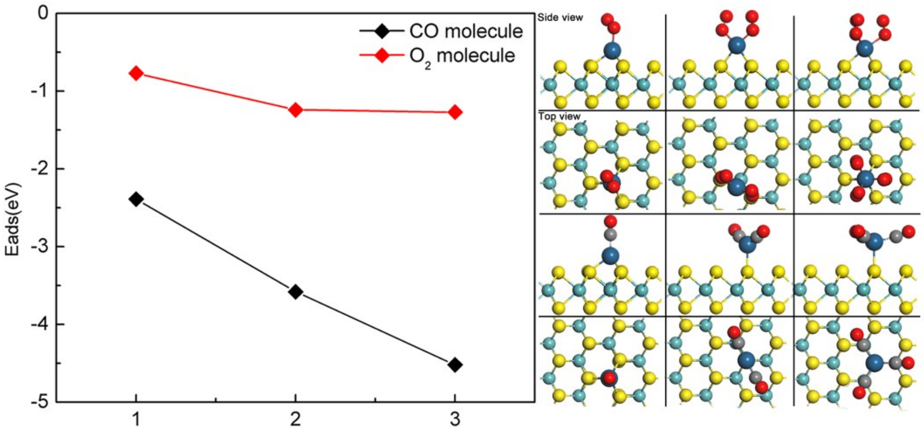

Fig.S2 The optimized adsorption configurations and corresponding adsorption energies of the multiple CO and O_2 molecule adsorption on a Pt/MoS_2 monolayer.

Table S2. The adsorption energy (E_{ads}) and structure information about the O_2 and CO adsorption on the Pt/MoS_2.

Species	E_{ads}/molecule (eV)	Bonding details	
		Bond	Distance (Å)
O_2	-0.77	O_a-O_b	1.26
		O_a-Pt	2.10
		O_b-Pt	3.35
		Pt-S	2.39
$2O_2$	-0.62	O_a-O_b	1.27
		O_a-Pt	2.07
		O_b-Pt	2.90
		Pt-S	2.42
$3O_2$	-0.42	O_a-O_b	1.26
		O_a-Pt	2.20
		O_b-Pt	2.98
		Pt-S	2.48
CO	-2.39	C-O	1.16
		C-Pt	1.88
		Pt-S	2.42
2CO	-1.79	C-O	1.16
		C-Pt	1.19
		Pt-S	2.49

3CO	-1.51	C-O	1.16
		C-Pt	1.95
		Pt-S	2.56

S4. The O_2 molecule dissociation on the Pt/MoS_2 surface

In order to evaluate the activation energy for O_2 dissociation alone in the absence of pre-adsorbed CO, the TS search for breaking the O-O bond of the O_2 molecule adsorbed on the Pt/MoS_2 catalyst monolayer is also investigated. Here in Figure S3, the configuration of the O_2 adsorption on Pt/MoS_2 structure (Initial states), the transition state (TS) and the dissociated O_2 adsorbed on Pt/MoS_2 (FS) are shown respectively. The activation energy for O_2 dissociation on Pt/MoS_2 is -1.44eV, which means that this process is very unlikely to occur at room temperature. The schematic energy profiles in the E-R mechanism along the minimum-energy pathway (MEP) through the $O_2 \rightarrow$O-O route are shown below. The O_2 dissociation with pre-adsorbed CO is described in Fig. 3 (p13), the activation barrier is only 0.40 eV. The dissociation of CO in absence of pre-adsorbed O atom on Pt/MoS_2 has also been considered, the product of this process i.e. C-Pt/MoS_2-O, is unstable.

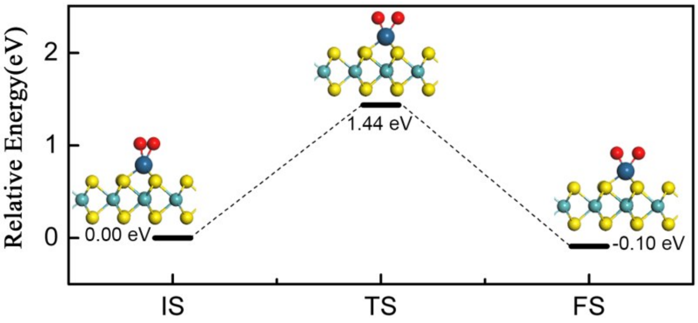

Fig.S3 The optimized adsorption configurations and corresponding activation energy of the O2 molecule dissociation on a Pt/MoS_2 monolayer

S5. The E-R mechanism as the first step of the CO oxidation

The free energy profile and steps involved in the E-R reaction for the first step of reaction of the CO oxidation is studied as follows. In the initial state, a CO molecule is put in close proximity to a pre-adsorbed O_2 over the Pt/MoS_2. The final state is set to be a CO_2 molecule in a vacuum and an atomic O adsorbed on the Pt/MoS_2. The corresponding activation barrier is 0.63 eV for O_2 dissociation and 0.62 eV for the subsequent CO_2 desorption. The L-H mechanism as the first step is about 0.23 eV lower than the E-R mechanism. We, therefore, assume that the L-H reaction as the first step dominates the catalytic process. One hundred structural images are inserted to initial states (IS) and the final states (MS), metastable state (MS) and final state (FS) respectively in order to accurately determine the minimum-energy pathway (MEP). Figure S4 shows the free energy profile and steps involved in the E-R reaction as the first reaction of the CO oxidation.

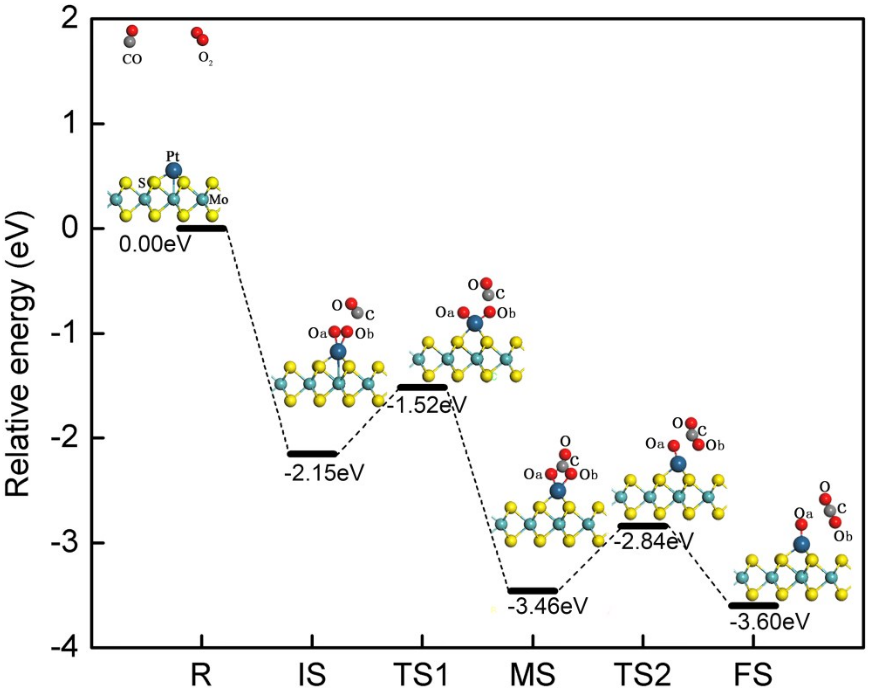

Fig. S4 Schematic energy profiles in the E-R mechanism along the minimum-energy pathway (MEP) through the CO+O_2→OOCO→CO_2+O route. The corresponding local configurations of the adsorbents on the Pt/MoS_2 catalyst at the initial state (IS), transition state (TS), metastable state (MS) and final state (FS) are also presented.

S6. The Mayer bond order analysis of the O_2 co-adsorbed on the Pt/MoS_2 monolayer

At this configuration, the O_a-O_b bond is stretched from 1.23 Å (O_2 in gas phase) to 1.40 Å, with the Mayer bond order of O_a-O_b decreasing from 2.02 (O_2 in gas phase) to 1.18 as shown in Figure S5 (a). Moreover, charge analysis shows that the O_2 molecule gains 0.53 |e| from the catalyst and forms covalent Pt-O bonds (the Mayer bond order values are 0.62 and 0.57 respectively), indicating that the O_2 molecule is chemically bonded to the Pt atom. The obtained negative charge fills in the HOMO orbital (shown in Fig. 2(g)), and leads to the non-spin polarized O_2 state, as shown in the projected density of states (PDOS) of Figure S5 (b).

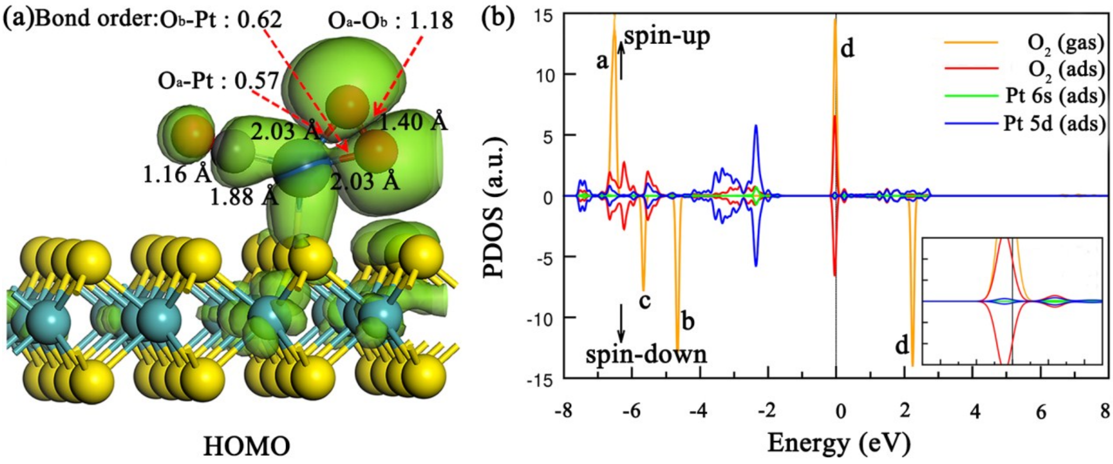

Fig. S5 (a) The HOMO distribution, Mayer bond orders and charge transfer (QT) between Pt and gas molecules & (b) projected density of states (PDOS) of the O_2, CO co-adsorption configuration.

S7. Diffusion of the Pt single atom on the Pt/MoS_2 monolayer

DFT calculations have been performed for Pt dimer adsorption on the MoS_2 substrate, the most stable configuration is two Pt atoms adsorbing above two HMo (hollow) sites. Since the calculated diffusion barrier of Pt atom on the MoS_2 substrate is about 0.73 eV (0.33 eV larger than the activation barrier of CO oxidation), it is hard for Pt atoms to cluster on the surface of MoS_2 monolayer.

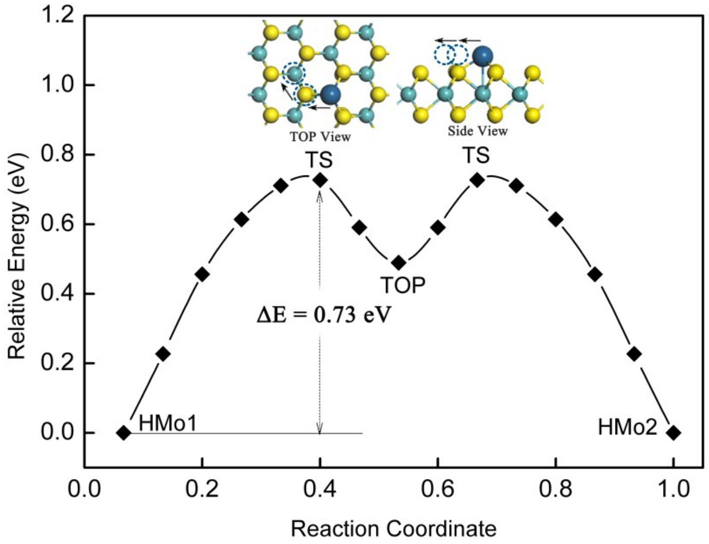

Fig. S6 The energy profile of the diffusion of the Pt single atom on the surface of the MoS_2 monolayer

S8. Configuration of the Pt dimmer adsorption on the Pt/MoS_2 monolayer

DFT calculations have been performed for Pt dimer adsorption on the MoS_2 substrate, the most stable configuration is two Pt atoms adsorbing above two HMo (hollow) sites as shown I Fig. S6 (a). For this configuration, the adsorption energy of the Pt dimer equals to the sum of adsorption energies of two isolated Pt atoms, indicating that the Pt-Pt interactions are negligibly small.

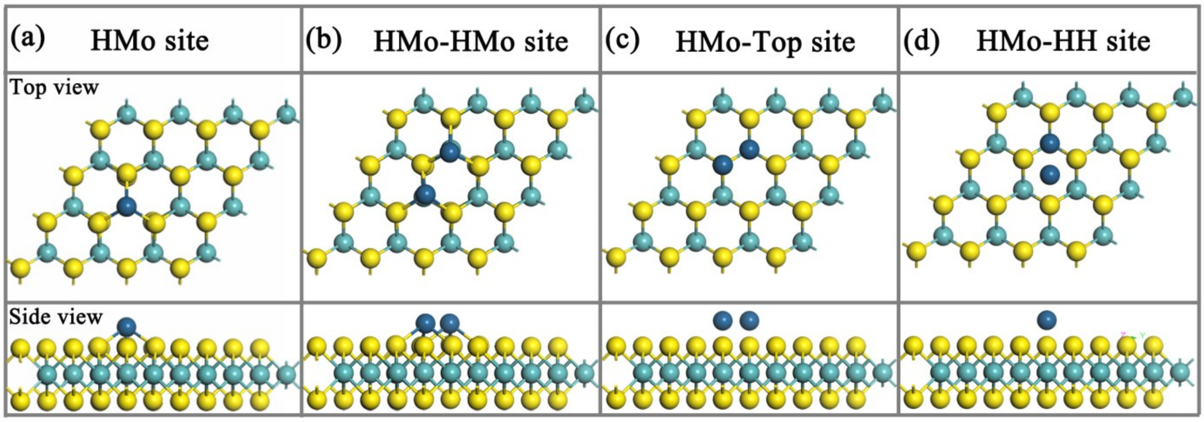

Fig. S7 The adsorption configurations of the Pt single atom and a Pt dimmer on the MoS_2 monolayer.

S9. Configuration of the Pt dimmer adsorption on the Pt/MoS_2 monolayer

As shown in Fig. S8a, the energy barrier for the second O_2 molecule adsorbs on the Pt/MoS_2 catalyst is 0.39 eV, indicating that the multiple O_2 adsorptions are plausible under the O_2-rich conditions. However, as shown in Fig. S8b, the activation barrier of replacing one of the O_2 with a CO molecule is only 0.22 eV, accompanied by an energy drop of 0.95eV. We, therefore, believe that the co-adsorption of a CO and an O_2 on Pt/MoS2 (the initial state of the L-H reaction) will be formed when the surface is exposed to the CO gas.

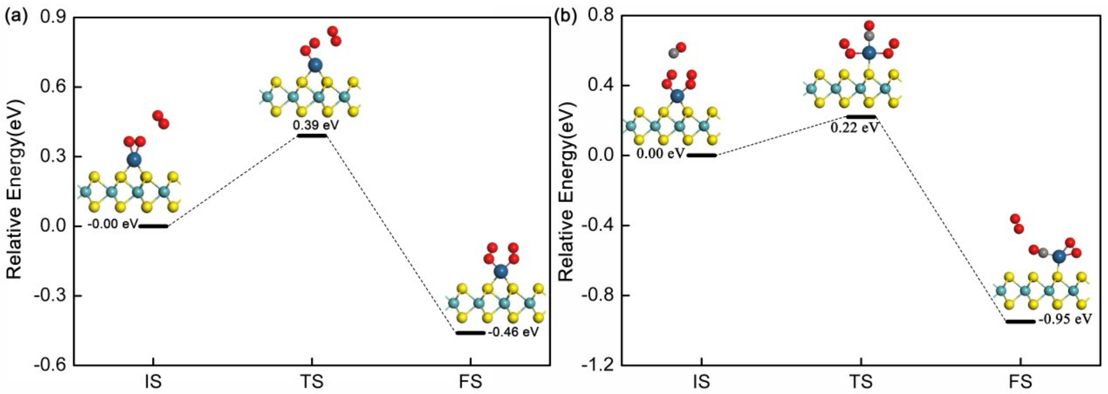

Fig. S8 (a) Schematic energy profiles of the co-adsorption of two O_2 molecules, and (b) replacing one O_2 molecule with a CO molecule.

Reference

1. D. Loffreda, D. Simon and P. Sautet, J.Chem.Phys, 1998, 108, 6447-6457.