First principles study of elemental mercury (Hg^0) adsorption on low index CoMnO_3 surfaces

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Abstract: The density functional theory (DFT) is applied to predict elemental mercury (Hg^0) adsorption on CoMnO_3 surface for the first time. GGA/PBE functional were selected to determine the potential Hg^0 capture mechanisms. The results show that Hg^0 has good affinity with CoMnO_3 surfaces with chemical adsorption. The adsorption energy of Hg^0 - CoMnO_3 (1 0 0), Hg^0 - CoMnO_3 (1 0 1) and Hg^0 - CoMnO_3 (1 1 0) are -85.225, -72.305 and -70.729 kJ/mol, respectively. The Hg-Mn and Hg-Co mechanisms were revealed on low index surfaces. Hg^0 was oxidized to its valence state of 0.236 on Mn site in CoMnO_3 (1 0 0) surface. The Hg-Co interaction mechanism occurred on Hg^0 - CoMnO_3 (1 0 1) and Hg^0 - CoMnO_3 (1 1 0) with $0.209e^-$ and $0.189e^-$ transformation, respectively. The PDOS analysis shows that Hg-Mn interaction depends on the hybridization of Hg(s- and d-orbitals) and Mn (s-, p- and d- orbitals). However, Hg-Co interaction stems from s- and d- orbitals of Hg, which only overlapping with d- and p- orbital of Co. Both the adsorption energy and electronic structure analysis indicated that CoMnO_3 catalyst performed excellent in Hg^0 oxidation. Exposing CoMnO_3 (1 0 0) is most favorable in Hg^0 control, which provides theoretical instruction on certain crystal plane synthesis in experiment.

Keywords: Elemental mercury; Electronic structure; PDOS; Density functional theory; Binding energy.

1. Introduction

Coal is primarily used as an essential solid fuel to produce electricity and provide heat through combustion. According to U.S. Energy Information Administration (EIA), world coal consumption was about 7.25 billion tons in 2010[1]. The utilization of coal leads to severe environment problems, such as mercury pollution in the air, which threatens our children and communities' health. Coal-fired power plants are the biggest anthropogenic sources of mercury release[2]. In the United State, power plants are currently the dominant emitters of mercury (50%). In China, burning coal contributes to 38% mercury emission. As mercury has adverse effects on the center nervous system (CNS) and causing neurodegeneration, many countries have made great efforts in its emission regulation. In 2011, the U.S. Environmental Protection Agency (EPA) regulated Mercury and Air Toxics Standards(MATS) to reduce mercury pollution from power plants[3]. In China, the regulation of mercury emission limit was $0.03\text{mg}/\text{Nm}^3$, a stricter limit of $0.003\text{mg}/\text{Nm}^3$ is expected in 2020[4]. In 2013, about 140 countries agreed in the Minamata Convention on Mercury by the United Nations Environment Program (UNEP) to prevent mercury emissions[5]. Mercury pollution control are facing special challenges worldwide. It is well known that coal derived flue gases has three kinds of mercury species including oxidized mercury (Hg^+ , Hg^{2+}), particle mercury(Hg^p) and elemental mercury(Hg^0). The former two mercury phases are

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readily removed from system by current air pollution control technologies, such as wet scrubber, wet flue gas desulfurization units[6-8] and electrostatic precipitators[9]. However, the control of Hg^0 is relatively difficult due to its high vapor pressure and low solubility [10-12]. Thus, it is compulsive and urgent to develop effective mercury sorbents using cost-effective methods.

Cobalt (Co) and manganese (Mn) based catalysts have aroused extensive concern of scholars due to their nature of the variable valence state. On the one hand, Mn-based sorbents has unique activity for capture/oxidation of Hg^0 depending on its redox couple $\text{Mn}^{3+}/\text{Mn}^{4+}$. Manganese dioxide (MnO_2) was used as active component doping on other carriers to control Hg^0 emission. For instance, Ji et al. [6] adopted $\text{MnO}_2/\text{TiO}_2$ catalysts in a fixed bed reactor to investigate Hg^0 adsorption activity. It revealed that Hg capture ability is linked with Mn loading amount and bed temperature. Besides, the catalysts of $\text{MnO}_2/\text{Al}_2\text{O}_3$ were applied for Hg capture from air carrier gases in a packed-bed reactor[13]. It exhibited high efficiency in Hg^0 adsorption. Furthermore, $\text{MnO}_2/\text{Al}_2\text{O}_3$ catalysts were also employed to remove Hg^0 from simulated flue gas via oxidation method[14]. Scala et al.[15] prepared a reusable sorbent MnO_2 impregnated on $\gamma\text{-Al}_2\text{O}_3$ for Hg^0 removal. It performs well up to 300°C and is completely regenerated at a temperature as low as 500°C . Wiatros-Motyka et al. [16] compared $\text{MnO}_2/\text{ZrO}_2$ with halogen impregnated activated carbons (AC) for the Hg^0 adsorption activity. It was found that $\text{MnO}_2/\text{ZrO}_2$ has much more capacity than that of AC. The results indicated that the catalysts have good performance in Hg^0 capture under an optimum at 230°C without HCl. Xu et al. [17] investigated $\text{MnO}_x/\text{graphene}$ composites for the capture of Hg^0 in flue gas, suggesting Mn as the active site. On the other hand, cobalt oxide (Co_3O_4) as a typical Co-based sorbent has highly active for Hg^0 oxidation due to its certain oxidation states of Co^{2+} and Co^{3+} . It was reported that Co^{3+} atoms have relative high oxidation ability playing as active site[18]. This catalyst has been investigated in mercury control for many years. Mei et al. [19] prepared Co_3O_4 modified AC for Hg^0 removal using a laboratory-scale fixed-bed reactor under simulated flue gases. Test showed that $\text{Co}_3\text{O}_4/\text{AC}$ could be regenerated through heating methods and eliminated Hg^0 secondary pollution. Subsequently, they investigated $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ composition to control Hg^0 . It was found that $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ has a greater oxidized mercury capture ability than Cl and Br doping $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ [20]. Liu et al. [21] conducted the Co/TiO_2 catalyst for Hg^0 control, which has higher Hg^0 oxidation activities in a temperature range of $120\text{-}330^\circ\text{C}$.

As mentioned above, both of MnO_2 and Co_3O_4 have remarkable merits in Hg^0 capture processes. The combination of these two catalysts were conducted in related studies[22]. However, pure Co-Mn double metal oxides have never been explored in Hg^0 control. It is still unknown if they have some important properties toward Hg^0 removal. Fortunately, Density function theory (DFT) calculation provides an economic efficiency method to predict the Hg^0 adsorption potential and possible mechanisms. The Hg^0 adsorption behaviors on MnO_2 (1 1 0)[23] and Co_3O_4 (1 1 0)[24] surfaces were investigated in previous studies, which are in consistent with experimental results. As far as we concerned, the related DFT research on cobalt manganese oxides catalysts for Hg^0 catalytic oxidation has rarely been reported. Hence, CoMnO_3 double-metal oxidation was chosen as a research object in this present study.

Our purpose is to reveal the potential catalytic of Hg^0 by CoMnO_3 using DFT predictions. We examine several low index surfaces of CoMnO_3 including CoMnO_3 (1 0 1) , CoMnO_3 (1 1 0) and CoMnO_3 (1 0 0) to investigate their average binding energy and adsorption energy. The possible

active sites were figured out. In addition, details of the structural and electronic properties are discussed. The partial density of states (PDOS) were analyzed systematically. This method provides Hg^0 adsorption behaviors on CoMnO_3 catalyst in molecular level. It also has positive effect on related crystal surface control, deciding beneficial plane exposing synthesis.

2. Method of calculation

2.1 Model construction

Cobalt Manganese(IV) Oxide (CoMnO_3) crystal is a trigonal/rhombohedral structure with space group R-3/R ($a=b=c=5.385\text{\AA}$, $\alpha=\beta=\gamma=54.52^\circ$, ICSD #31854)[25]. The primary cell is shown in **Fig.1**. Supercell approach was employed to construct low index CoMnO_3 crystal surfaces including CoMnO_3 (1 0 1), CoMnO_3 (1 1 0) and CoMnO_3 (1 0 0). The top and side view are shown in **Fig.2**. All of them are produced periodically in the space with surface area of $9.625 \times 10.493\text{\AA}^2$. Each surface contains 36 O atoms, 12 Mn atoms and 12 Co atoms. A vacuum thickness of $18\text{\AA}$ was chosen to eliminate neighboring slab interaction effects. The atom thickness was $1.509\text{\AA}$ with 60 atoms for three surfaces. The atom layers size of CoMnO_3 surface is six times larger than the primary cell. The bottom layer was constrained and the other layers were relaxed.

Fig.1 The primary cell of CoMnO_3 crystal

Fig.2 The configuration of three low index CoMnO_3 crystal surfaces

2.2 Calculation methods

All calculations of low index CoMnO_3 were performed using DMol³ package in Material Studio 70[26]. DMol³ is a modeling program that uses density functional theory (DFT) to simulate chemical processes and predict properties of materials. It produces highly accurate results, while

keeping the computational cost low for ab initio method. The accuracy of local and gradient-corrected functional compared before the calculation. Perdew-Burke-Ernzerhof (PBE) approximation described by a generalized gradient approximation (GGA) provides a better consistency with experimental lattice parameters. Therefore, GGA-PBE method was used as electron exchange correlation functionals. A double numerical basis with polarization functions (DNP) were chosen in the calculations[27]. As for core treatment, all electron was used for O atom. DFT Semi-core PseudoPotentials (DSPP)[28] were used for Hg, Mn and Co atoms. The inner electrons of these atoms were as a simple potential including some degree of relativistic effects and the outer electrons were treated as valence electrons. In addition, an orbital cutoff of 4.7Å was used in CoMnO₃ surfaces and Hg⁰-CoMnO₃ system. The self-consistent field convergence criterion was set to an energy change of 10⁻⁶Ha. The Brillouin Zone integrations were performed using 6×6×6 and 2×3×1 Monkhorst-Pack grid for bulk lattice optimization and Hg⁰ adsorption system, respectively. The convergence tolerance of geometry optimization based on energy, maximum force and maximum displacement were 1×10⁻⁵Ha, 2×10⁻³Ha/Å and 5×10⁻³Å, respectively. The spin polarization was applied in all calculations.

2.3 Binding energy

Binding energy is the energy required to disassemble a whole system into separate parts. A bound system typically has a lower potential energy than the sum of its constituent parts: this is what keeps the system together. Often this means that energy is released upon the creation of a bound state. This definition corresponds to a positive binding energy. In terms of different slabs, the average binding energy $E_{binding}$ is defined as:

$$E_{binding} = \frac{n_{Co}E_{Co} + n_{Mn}E_{Mn} + n_OE_O - E_{total}}{n_{Co} + n_{Mn} + n_O} \quad (\text{Eq. A})$$

where n_{Co} , n_{Mn} and n_O are the number of Co, Mn and O atoms within the slab, E_{Co} , E_{Mn} and E_O corresponding to their total energy, E_{total} is the total energy of the slab.

2.4 Adsorption energy

For adsorption energy, it was calculated according to the following equation:

$$E_{ads} = E_{Hg^0+surface} - E_{Hg^0} - E_{surface} \quad (\text{Eq. B})$$

where E_{ads} is the adsorption energy, $E_{Hg^0+surface}$ represents the energy of the adsorption system,

E_{Hg^0} is the energy of the element mercury, $E_{surface}$ is the energy of periodic surface, all energies are in kJ/mol. By this definition, negative value corresponds to exothermic adsorption process.

3. Results and discussion

3.1 DFT methods comparison

To confirm which DFT method can provides more reliable calculation results, different functional methods (LDA-PWC, GGA-PBE and GGA-BLYP) were used in primary CoMnO₃ crystal optimization. All lattice parameters of bulk CoMnO₃ after optimization were listed in **Table 1**. From respect of various direction cell lengths, all methods have underestimated this

parameter. The GGA-BLYP method has the largest relative tolerance of 7.130%, followed by LDA-PWC method with 5.098% relative tolerance. The GGA-PBE method exhibits best performance in predicting cell lengths. It has only 2.582% relative tolerance with length error of 0.139 Å. With respect of cell angles, the selected methods have overestimated this parameter. The method of GGA-BLYP has the highest relative tolerance corresponding to 7.332%. LDA-PWC and GGA-PBE methods have lower relative tolerance (2.733%), which indicates acceptable in error.

Table 1 The optimized lattice parameters of different DFT methods

Lattice parameters	Exp. values	LDA-PWC		GGA-PBE		GGA-BLYP	
		Values	RT (%)	Values	RT (%)	Values	RT (%)
a	5.385 Å	5.154 Å	4.281	5.261 Å	2.310	5.001 Å	7.130
b	5.385 Å	5.110 Å	5.098	5.246 Å	2.582	5.276 Å	2.028
c	5.385 Å	5.172 Å	3.947	5.378 Å	0.137	5.403 Å	0.334
α	54.520°	55.311°	1.450	54.205°	0.577	52.145°	4.356
β	54.520°	55.237°	1.315	55.509°	1.814	58.518°	7.332
γ	54.520°	55.931°	2.589	56.010°	2.733	55.715°	2.193

Note: Exp. = Experimental[25]; RT=Relative tolerance.

In previous DFT studies, GGA-PBE method was employed in Mn or Co elements contained metal oxidize system which showed reasonable accuracy [23, 29]. This method also had good performance in bulk CoMnO₃. Considering all these aspects, GGA-PBE method was chosen in the following parts.

3.2 Low index CoMnO₃ surfaces vacuum thickness

Table 2 The energy differences of various vacuum thickness (unit: eV)

Surface types	$\Delta E(13\text{\AA}-16\text{\AA})$	$\Delta E(16\text{\AA}-18\text{\AA})$	$\Delta E(18\text{\AA}-20\text{\AA})$
CoMnO ₃ (1 0 1)	0.025	0.009	-0.007
CoMnO ₃ (1 1 0)	0.025	0.009	-0.007
CoMnO ₃ (1 0 0)	0.022	0.009	0.112

Three low index CoMnO₃ surfaces, CoMnO₃ (1 0 1), CoMnO₃ (1 1 0) and CoMnO₃ (1 0 0), were constructed by supercell approach. It is essential to eliminate related effects between slabs. Hence, four vacuum thicknesses were investigated in determining a reasonable height. The total energy of low index surfaces under different vacuum thicknesses are compared. The energy differences are shown in **Table 2**. The energy difference between 13 Å and 16 Å are in the range of 0.022-0.024 eV. When the vacuum thickness increased to 18 Å, the energy difference between 18 Å and 16 Å decreased to 0.009 eV. The energy difference between 18 Å and 20 Å further decrease to 0.007 eV for CoMnO₃ (101) and (1 1 0), while it increased to 0.112 eV for CoMnO₃ (100). These energy differences were acceptable. Therefore, the suitable vacuum height was set to 18 Å for three low index surfaces. This height is sufficient to ignore nearby slab interaction. All Hg⁰ adsorption calculation were carried out under this condition.

3.3 Binding energy and adsorption energy

Table 3 The average binding energy of low index CoMnO₃ surfaces

Low index surfaces	Binding energy (eV)
CoMnO ₃ (1 0 1)	9.290
CoMnO ₃ (1 1 0)	9.290

The average binding energy of CoMnO₃ (1 0 1), CoMnO₃ (1 1 0) and CoMnO₃ (1 0 0) surfaces are shown in **Table 3**. Both CoMnO₃ (1 0 1) and CoMnO₃ (1 1 0) surfaces binding energy are 9.290eV. The binding energy of CoMnO₃ (1 0 0) is 9.281eV with deviation of 0.009eV comparing to former two surfaces. It suggests that all of them have stable structure. Hence, CoMnO₃ (1 1 0), CoMnO₃ (1 0 0) and CoMnO₃ (1 0 1) were considered in the following calculation regarding of Hg⁰ adsorption.

Table 4 Adsorption properties of Hg⁰ on low index CoMnO₃ surfaces

Adsorption system	Adsorption energy (kJ/mol)	Distance(Hg-bonded atoms) (Å)	Distance (Hg-surface) (Å)
Hg ⁰ -CoMnO ₃ (1 0 0)	-85.225	2.938	1.968
Hg ⁰ -CoMnO ₃ (1 0 1)	-72.305	2.736	2.694
Hg ⁰ -CoMnO ₃ (1 1 0)	-70.729	2.744	2.739

We built three adsorption systems to study the interaction behavior of Hg⁰ on CoMnO₃ surfaces. Several sites including Mn, Co and O atoms were chosen to investigate which one is active on the surface. The optimized structures of all situations in each system are presented in **Fig. 3**, and the adsorption energies of Hg⁰ on the surface, the distance between Hg and bonded atoms are summarized in **Table 4**. The atom of Mn is the active site for Hg⁰ adsorption on CoMnO₃ (1 0 0) surface. Hg⁰ prefers to adsorb on Co atom on the surface of CoMnO₃ (1 0 1) and CoMnO₃ (1 1 0). From the calculated adsorption energy, all systems have negative values of adsorption energy indicating that the adsorption of Hg⁰ on CoMnO₃ surfaces is exothermic. The Hg⁰-CoMnO₃ adsorption system is attributed to metal atoms dominating active site, which is consistent with Hg⁰-Fe₂O₃[30] and Hg⁰-CuO[31] interaction system. Surface metal atoms have good affinity with Hg⁰.

The Hg⁰ adsorption on CoMnO₃ (1 0 0), CoMnO₃ (1 0 1) and CoMnO₃ (1 1 0) are chemical adsorption with adsorption energy of -85.225, -72.305 and -70.729 kJ/mol, respectively. There is a growing trend towards the distance between Hg and related surfaces. The distance results were ranked in ascending order as follows: Hg⁰-CoMnO₃ (1 0 0) (1.968 Å) < Hg⁰-CoMnO₃ (1 0 1) (2.694 Å) < Hg⁰-CoMnO₃ (1 1 0) (2.932 Å). Higher distance corresponds to lower adsorption energy, and vice versa. The bond length of mercury and bonded atoms reveals the strength of the bond stability. Hg-Mn bond is higher than Hg-Co bond in value. The former has 2.938 Å in length; the latter two are 2.736 Å and 2.744 Å.

We have conducted Hg⁰ adsorption on Co₃O₄ (1 1 0) surface which has adsorption energy of -74.037kJ/mol. It indicates that CoMnO₃ surface is superior to Co₃O₄. Taking adsorption energy and length parameters into consideration, CoMnO₃ (1 0 0) is the most favorable face for Hg⁰ adsorption, followed by CoMnO₃ (1 0 1) and CoMnO₃ (1 1 0). The atom of Mn has stronger interaction with Hg⁰ than that of Co atom. It may be attributed to the differences in valence states of Mn (+2, +3 and +4) which has greater potential than Co in obtaining electrons from Hg⁰.

3.4 Electronic structure

3.4.1 Electrons transfer

Hg-CoMnO₃(1 0 0) surface

Hg-CoMnO₃(1 0 1) surface

Fig.3 The optimized structure and atomic indexes of each adsorption system

Electrons transfer is an essential criterion, which allows for deeper understanding of the interaction between Hg^0 and CoMnO_3 surfaces. Atoms of top layers are taken into consideration using population analysis. Mulliken and Hirshfeld charge partitioning methods are integrated in DMol³ module which are essential population analysis approaches. Fonseca Guerra et al. have assessed the Mulliken, Bader, Hirshfeld, Weinhold and Voronoi deformation density (VDD) methods for charge analysis. According to their assessment results, the Mulliken charge has heavy basis set dependency that resulted in the unstable electrons interaction. The Hirshfeld charge, which proved to be numerically very similar, was recommended because it provided chemically meaningful charges. Hence, the Hirshfeld method was adopted in obtaining atoms charge before and after adsorption. All adsorption system atoms indexes are labeled in **Fig.3** and obvious charge differences are summarized in **Table 5**.

Hg^0 adsorbed on CoMnO_3 (1 0 0) surface was attributed to Hg-Mn interaction mechanism. Electrons are shifting from Hg^0 to (1 0 0) plane after adsorption. It is reasonable that metallic atoms (Co, Mn) exhibits positive valence state and O atom showed negative states. The Hg^0 denotes $0.236e^-$ to the slab and turns to oxidized mercury. The bonded atom Mn (60) gets $0.078e^-$, which is the biggest one among slab atoms. Top layer Co and Mn atoms has essential roles in electrons transfer. The charge transfer of Mn (30) and Co (45) atoms are $0.031e^-$ and $0.045e^-$, respectively. The atom of O (5) gain $0.021e^-$ from other atoms. Less electrons transfer occurred among remaining atoms.

Both of Hg^0 adsorption on CoMnO_3 (1 0 1) and CoMnO_3 (1 1 0) slabs are Co site dependent interaction. The Hg^0 denotes $0.209e^-$ to (1 0 1) surface. The maximum electrons acceptor is Co (11) with $0.085e^-$, which bonded with Hg atom. Other typical top atoms, such as Mn (15), Mn (45) and

Co (26), their electron transfer in descending order are as follows: $0.022e^- > 0.019e^- > 0.014e^-$. All other atoms have no obvious electron flow. Hg^0 was oxidized to valence state with charge of $0.189e^-$ after adsorption on (1 1 0) plane. The atom of Co (26) gains $0.095e^-$ and forms Hg-Co bond in a stable state. Then, surplus electrons from Hg^0 transport to other atoms. For example, Mn (60), Mn (45) and Mn (15) accept $0.018e^-$, $0.017e^-$ and $0.011e^-$, respectively. Especially in bottom layers, less than $0.010e^-$ transport among other atoms.

Table 5 The charge transfer of Hg^0 -CoMnO₃ low index surface systems

Atomic index	Hg ⁰ -CoMnO ₃ (1 0 0) system Charge transfer	Hg ⁰ -CoMnO ₃ (1 0 1) system Charge transfer	Hg ⁰ -CoMnO ₃ (1 1 0) system Charge transfer
O (5)	0.021	0.000	0.002
O (9)	0.015	0.002	0.002
Co (11)	0.001	0.085	0.010
Mn (15)	0.006	0.022	0.011
O (16)	-0.014	0.001	-0.001
O (19)	0.013	-0.002	0.004
O (24)	0.013	-0.001	0.003
Co (26)	-0.002	0.014	0.095
Mn (27)	-0.015	0.001	0.010
Mn (30)	0.031	0.005	0.004
O (34)	0.013	-0.001	0.003
O (39)	0.013	-0.001	0.002
Co (41)	-0.002	0.012	0.004
Mn (42)	-0.015	0.004	-0.005
Mn (45)	0.007	0.019	0.017
Co (56)	-0.004	0.010	0.007
Mn (57)	-0.016	0.002	-0.004
Co (58)	0.045	-0.001	0.003
Mn (60)	0.078	0.005	0.018
Hg (61)	-0.236	-0.209	-0.189

From the result obtained, Hg^0 has strong electron transfer interaction with CoMnO₃ surfaces. Higher mercury oxidation states leads to stronger adsorption energy and electrons flow among surface atoms. Metallic atoms play important role in electron transfer process, which have great potential in electron receiving and donating. The Mn active site is more favorable than that of Co site adsorption.

3.4.2 Partial density of states

The bonding strength between adsorbate and surface atoms can be analyzed by comparing the degree of overlapping between the PDOS peaks and their positions with respect to the Fermi level. To make better comparison, the adsorption system based on Mn and Co sites of Hg^0 -CoMnO₃ (1 0 0), Hg^0 -CoMnO₃ (1 0 1) and Hg^0 -CoMnO₃ (1 1 0) are shown in **Fig.4**, **Fig.5** and **Fig.6**, respectively. In terms of individual Hg atom, s- and d- orbitals peak locate near 0.478Ha and -0.112Ha, respectively. Unoccupied p- orbital distributes in 0.258Ha. They shift to lower energy area with smaller PDOS peak after adsorption due to the charge transfer from the Hg to Mn or Co atoms of the surface.

Fig.4 PDOS for surface system before and after Hg^0 adsorption on Mn sites of $\text{CoMnO}_3(100)$ surface. The solid thin lines represent before adsorption, and solid thick lines represent after adsorption. (a) is for Hg atom and (b) is for bonded Mn atom.

In **Fig.4 (a)** for Hg atom, the peak of s- orbital move to -0.084Ha with value of 36.907 electrons/Ha. The peak of d- orbital shift to -0.202Ha with value of 353.783 electrons/Ha. PDOS of s- and d- orbitals showed the decrease of 75.061 electrons/Ha and 206.058 electrons/Ha, respectively. The orbitals of Mn atom have a reverse tendency with that of Hg after adsorption. In **Fig.4 (b)**, peaks of PDOS increased and the energy distribution was in higher level. After adsorption, PDOS peaks of s- orbital in energy moves from -0.712Ha , -0.665Ha , -0.247Ha and 0.025Ha to -0.698Ha , -0.658Ha , -0.219Ha and 0.033Ha , respectively. The highest PDOS (difference between the peaks before adsorption and after adsorption) of s- orbital reaches 0.845electrons/Ha . PDOS energy distribution of p- orbital turns from -0.699Ha , -0.655Ha , -0.217Ha , -0.137Ha , -0.044Ha and 0.022Ha to -0.693Ha , -0.649Ha , -0.212Ha , -0.140Ha , -0.013Ha and 0.033Ha , respectively. The biggest PDOS incrementation is 1.168electrons/Ha . Slight changes have been observed in d-orbital before and after adsorption. Their PDOS and energy coordinates turn from $(0.031\text{Ha}, 27.746\text{electrons/Ha})$ to $(0.036\text{ Ha}, 35.862\text{ electrons/Ha})$. The largest PDOS is as high as 8.116electrons/Ha . It indicates that Mn has accept certain amount of electrons leading to the increase of system energy. Considering the orbital energy peak overlapping of related atoms, orbitals (s-, d-) of Hg atom and orbitals (s-, p- and d-) of Mn atom are hybridized in -0.084 Ha and -0.202 Ha , respectively. It reveals that Hg has strong interaction with Mn atom orbitals. This is consistent with the results of adsorption energy and charge transfer between Hg and surface Mn atom.

Fig.5 PDOS for surface system before and after Hg^0 adsorption on Co sites of $\text{CoMnO}_3(101)$ surface. The solid thin lines represent before adsorption, and solid thick lines represent after adsorption. (a) is for Hg atom and (b) is for bonded Co atom.

In **Fig.5 (a)** for Hg atom, PDOS peak of s- orbital shift to energy -0.091Ha with $51.915\text{electrons/Ha}$ after adsorption. PDOS peak d- orbital reaches $405.450\text{electrons/Ha}$ at energy of -0.205Ha in stable state. As shown in **Fig.5 (b)** for Co atom, PDOS of all orbitals has increased with energy migration after adsorption. Specifically, s- orbital energy-PDOS coordinates moves from $(-0.255\text{Ha}, 5.236\text{electrons/Ha})$ and $(-0.013\text{ Ha}, 1.841\text{ electrons/Ha})$ to $(-0.261\text{Ha}, 6.756\text{electrons/Ha})$ and $(0.001\text{ Ha}, 1.389\text{ electrons/Ha})$, respectively. The largest PDOS incensement is 1.520electrons/Ha . The energy of p- orbital shifts from -0.237Ha to -0.217Ha with PDOS increase of 0.978electrons/Ha . The d- orbital distributes in energy range of $-0.190\text{-}0.033\text{Ha}$. PDOS peak value is raised from $112.984\text{ electrons/Ha}$ to $131.511\text{ electrons/Ha}$ with $18.527\text{ electrons/Ha}$ increment. Hg s- orbital is overlapping with Co p- orbital near -0.091Ha indicating the hybridized interaction. The d- orbital of Hg hybridized with Co orbitals (s- and p-) near -0.205Ha .

Fig.6 PDOS for surface system before and after Hg^0 adsorption on Co sites of $\text{CoMnO}_3(110)$ surface. The solid thin lines represent before adsorption, and solid thick lines represent after adsorption. (a) is for Hg atom and (b) is for bonded Co atom.

In **Fig.6 (a)** for Hg atom, peaks of s- and d- orbitals (Hg) locate in -0.085Ha and -0.205Ha after adsorption, respectively. The corresponding PDOS are $52.002\text{ electrons/Ha}$ (s- orbital) and $405.450\text{ electrons/Ha}$ (p- orbital). In terms of Co atom, as shown in **Fig.6 (b)**, no significant shifts can be observed in PDOS curves after interaction. The s- orbital has maximum energy change of 0.012Ha with biggest PDOS difference of 0.033electrons/Ha . Besides, p- orbital has maximum energy differences of 0.027Ha and maximum PDOS differences of 0.831electrons/Ha . The change of energy and PDOS for d- orbital are 0.003Ha and $23.912\text{electrons/Ha}$, respectively. From respect of PDOS overlap region, Hg (s- and d- orbitals) has hybridization with Co (p- orbital), which enhances the adsorption system substantially.

4. Conclusions

Spin unrestricted DFT calculation was employed to understand the possible mechanisms of Hg^0 on $\text{CoMnO}_3(100)$, $\text{CoMnO}_3(101)$ and $\text{CoMnO}_3(110)$ surfaces. The functional of

GGA-PBE exhibited best accuracy in predicting CoMnO₃ lattice parameters. The surface of CoMnO₃ (1 0 0) is the most beneficial for Hg⁰ adsorption. The atom of Mn has stronger interaction with Hg⁰ than that of Co atom. Exposure of CoMnO₃ (1 0 0) surface is favorable in Hg⁰ removal. The interaction of Hg⁰-CoMnO₃ (1 0 0) system attributed to chemisorption with adsorption energy of -85.225 kJ/mol and 0.236e⁻ transformation. The partial density of states (PDOS) showed that all orbitals of Hg moved to lower energy area after adsorption due to electron transfer. As for Hg-Mn mechanism, s- and d- orbitals of Hg have overlapped with all orbitals of Mn atom at certain energy states further confirming the stable adsorption process. Nevertheless, Hg-Co mechanism depends on Hg⁰(s-and d- orbitals) hybridization with Co (p- and d- orbitals). This study provides theoretical prediction towards CoMnO₃ based adsorbents with Hg⁰. Based on adsorption energy, CoMnO₃ is superior to Co₃O₄ surface. It is beneficial to prepare and design high efficient Hg⁰ controlling materials.

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