NH$_3$ adsorption on PtM (Fe, Co, Ni) surfaces: cooperating effects of charge transfer, magnetic ordering and lattice strain

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Abstract

Adsorption of a molecule or group with an atom which is less electronegative than oxygen (O) and directly interacting with the surface is very relevant to development of PtM (M=3d-transition metal) catalysts with high activity. Here, we present theoretical analysis of the adsorption of NH$_3$ molecule (N being less electronegative than O) on (111) surfaces of PtM(Fe,Co,Ni) alloys using the first principles density functional approach. We find that, while NH$_3$-Pt interaction is stronger than that of NH$_3$ with the elemental M-surfaces, it is weaker than the strength of interaction of NH$_3$ with M-site on the surface of PtM alloy.

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point averaged over spin-up and spin-down d-band centers. therefore the effects of the spin polarization are neglected. In PtM alloys, the d band filling of the metals (M) are different from their parent state. The lattice mismatch between the M-Pt results a strain in the system, which can also influence the catalytic activity.

To understand the possibility of selective M-coverage with N-containing ligand, we have studied the adsorption of NH$_3$ on PtM (Fe, Co, Ni) surfaces. Our calculations reveals a reversibility of adsorption behaviour of NH$_3$ molecule on M sites of PtM in comparison to the pure M(Fe,Co,Ni) surfaces. NH$_3$ has larger adsorption energies on M-site of PtM surface than of an M-site of elemental surfaces. We relate the such changes in adsorption energies to the physical mechanisms such as charge transfer, magnetic moment and strain effects. Although the effects of charge transfer and strain can be related to the shift of the d-band center, the effect spin polarization is not included in the d-band model. Most prominently, we have quantified the effects of these mechanisms from our first-principles calculations. For designing highly efficient alloy catalysts such as PtM, we suggest that one should gather insights from a multicomponent descriptor rather than a scalar descriptor such as d-band center.

Our first-principles calculations were within the framework of density functional theory (DFT) with Perdew-Burke-Ernzerhof functional of exchange correlation energy derived within a generalized gradient approximation[^15] and projector augmented wave (PAW) method as implemented in Vienna *ab initio* simulation package (VASP)[^16]. The PAW potentials include the following valence electrons: 3d$^8$4s$^1$ for Co, 5d$^9$5s$^1$ for Pt, 2s$^2$2p$^3$ for N, and 1s$^1$ for H. Surfaces of Pt, M and PtM were simulated using periodic supercells containing slabs of their 4 $\times$ 4 $\times$ 1 k-points using Methfessel-Paxton smearing with a width of 0.1 eV. Ionic relaxation are performed such that the force on each ion is smaller than 0.02 eV/Å. The dipole correction was applied along the direction perpendicular to the metal surfaces to correct the electric fields arising from the structural asymmetry and periodicity. The adsorption energies were determined using the relation,

$$E_{ad} = E_{S+A} - (E_S + E_A),$$

where $E_{S+A}$ is the energy of the surface plus adsorbate while $E_S$ and $E_A$ are energies of the surface and adsorbate respectively. Magnetic interactions among M-M and M-Pt are considered to be ferromagnetic.

For each PtM alloy considered here, we first obtained its optimized structure for (1:1) composition. We optimized its structure with tetragonal symmetry with P4/mmm space group. In the optimized structure, (see Table. I), $\frac{a}{c} \simeq \sqrt{2}$, and M-atom occupies the 1a (0,0,0) site and Pt occupies 1d (0.5,0.5,0.5) site. It is known that the L1$_2$ phase become stable for FePt below 1300 °C, for CoPt below 825 °C and for NiPt below 1300 °C[^8]. The (111) surface was constructed from this relaxed bulk structure. In the Table II, we report the adsorption energies of NH$_3$ molecule on elemental metal surfaces as well as on MPt surfaces for the atop positions, which is the most preferred adsorption site for NH$_3$ on the transition metal surfaces[^9][^10][^11]. For the elemental metal surfaces, NH$_3$ has highest adsorption energy on Pt (111) surface followed by Ni (111), Fe (110) and Co (0001). However, on MPt surfaces NH$_3$ is found to have stronger binding at M sites than Pt. The strength of NH$_3$-Pt binding on MPt surfaces decrease as we move from Ni to Fe. Such reversal of adsorption behaviour is interesting and also give us scope for tuning the activity of PtM alloy through manipulating the electronic structure of M-sites using suitable ligands. The question is: how do we understand such reversal of chemisorption?

From the average magnetic moments at the M-sites in PtM surfaces and those in the pure M-surfaces (shown in bracket in the Table I), we see that the magnetic moments on M-sites are larger in PtM than in pure M. This is due to charge transfer from the minority d-band of M to d-band of Pt as is evident in spin-resolved Bader charges[^12] reported in Table III. It is seen that about 0.82 electrons transfer from Fe-d bands to Pt d-bands, of which is 0.45 electrons transfer to the majority spin channel and 0.37 electrons are transfer to the down spin channel of the Pt-d bands. Similarly, 0.48 electrons transfer from Co site to the Pt site, of which 0.41 electrons transfer to the majority spin channel and only 0.07 electrons of Pt-d band. In the case of NiPt, 0.34 electrons transfer from Ni to Pt, out of which 0.31 electrons are transferred to the majority Pt-d band and only 0.03 electrons transfer to Pt minority d-band. This charge transfer also induces a small magnetic moment on the Pt atom, the magnitude of the magnetic moment being 0.5, 0.45 and 0.34 μ$_B$ respectively for FePt, CoPt and NiPt.

From the optimized lattice constants (Table. I) we expect strain effects, as reflected in the magnitude of the surface vectors for the pure metal (M) as well as PtM surfaces (Table. IV), it is clear that the M-M distances are longer for
PtM than that in pure M surface (by about 8% for Fe, 6% for Co and 7% for Ni). According to the d-band model of heterogeneous catalysts, for the late transition metals such as Fe, Co and Ni the increase in inter atomic distance for M lattice leads to narrowing of M d-band width which will cause the increase in the strength of chemisorption due to an upward shift of the d-band center to preserve the charge conservation[13].

From the projected density of states (DOS), it is clear that the majority spin d-bands are completely full in FePt and CoPt and determine the M-magnetic moment while magnetic moment is determined by both majority and minority spin electrons in NiPt.

In pure metallic surfaces there is no inter-site charge transfer since there is no difference in the electronegativity among these sites. However for the PtM systems there is charge transfer effect arising from the difference in the electron negativity of M and Pt atoms. On the Pauling scale, the electronegativity difference between Pt and M (Fe, Co, Pt) are 0.45, 0.40, 0.37 respectively. The magnetic moments on M-sites in PtM surfaces are in general larger than what is there in M-sites in a pure M-surface. Also there are strain effects in due to the lattice mismatch between Pt and M in PtM. The difference in the adsorption energy of NH3 molecule from M to the PtM surfaces arise due to a combined effects of the above mentioned phenomena. To uncover the individual contributions of charge transfer, magnetism and strain we apply the following methodology.

The adsorption energy of the NH3 molecule on the M surface is given by,

$$E_{ad}^M = E_{M+\Delta} - E_M - E_A$$

while that on a PtM surface is written as,

$$E_{ad}^{PtM} = E_{PtM+\Delta} - E_{PtM} - E_A$$

The change of the adsorption energy of NH3 molecule from the M to PtM surface can be written as[9]

$$\Delta E_{ad} = E_{ad}^{PtM} - E_{ad}^M = (E_{PtM+\Delta} - E_{M+\Delta}) - (E_{PtM} - E_M)$$

$$= \Delta E_q + \Delta E_m + \Delta E_e,$$  \hspace{1cm} (4)

where $\Delta E_q$, $\Delta E_m$ and $\Delta E_e$ are respectively the contributions to the changes in adsorption energy $\Delta E_{ad}$ coming from the charge transfer, magnetic moments and strain. To calculate $\Delta E_q$, $\Delta E_m$ and $\Delta E_e$ we have used following method: We assume that one can simulate the effects of Pt-coordination on M, by considering the pure M surface with an enhanced surface area (to capture the effect of strain), a larger magnetic moment and a less number of electrons per M atom. We express such assumptions in a mathematical form given by,

$$\Delta E_q = E_q^M(S_{PtM}) - E_q^M(S_M)$$

$$\Delta E_m = E_m^M|m_{PtM}| - E_m^M|m_M|$$

$$\Delta E_e = E_e^M(q_{PtM}) - E_e^M(q_M)$$

(5)

$\Delta E_e$ involves calculation of adsorption energy of NH3 on the M-surface at its equilibrium surface area $S_M$ and on the M-surface with enhanced surface area $S_{PtM}$ (which is the surface area of PtM). To obtain $\Delta E_m$, we perform calculation of adsorption energies for the M-surface with an enhanced magnetic moment, by co-straining the overall magnetic moment of the system such that the magnetic moment per M ion is about $m_{PtM}$ (which is the magnetic moment per M ion in a PtM surface). Since there is no change in the electronic charge inside the M sphere (only redistribution of majority and minority spin electrons), no charge transfer effect is involved. Also since the structure is unchanged, the strain effects is absent too. The last term of the Eq.5 ($\Delta E_q$) is obtained by subtracting the magnetic and lattice contributions from the total $\Delta E_{ad}$ (from the Eq.(4)).

Using the methodologies above, we have split the $\Delta E_{ad}$ into its lattice, magnetic and charge transfer contributions (see table tabulated in Table. IV). It is seen that for FePt and CoPt the increase of NH3 adsorption energy w.r.t the Fe and Co surface can be related mostly to the strain and the charge transfer effects, magnetism plays weaker role here. For NiPt, due to relative smaller difference of electro negativity between Ni and Pt the charge transfer effect is small. The change in adsorption energy is mainly dominated by strain effect. Also, among all three, FePt is expected to be best in terms of activity since the selective M-coverge with NH3 is easiest in this case.
In the Fig.2, we show the DOS of NH\textsubscript{3} in the gas phase (2a), the Co-d projected DOS and NH\textsubscript{3} projected DOS for NH\textsubscript{3} adsorbed Co (0001) surface (2b) and d-projected DOS for the Co (0001) surface (2c). From 2(a) and 2(c) it is evident that the lowest unoccupied levels (4a1,2e levels) of NH\textsubscript{3} are well above the d-states and are weakly involved in the chemisorption. It is the non-bonding lone pair (3a1 level) which describes the M-NH\textsubscript{3} bonding. On the metal surface the lone pair is highly stabilized (by about 4 eV), while the three NH\textsubscript{3} bonds (doubly degenerated 1e level and 2a1 level) are also stabilized slightly.

Since NH\textsubscript{3} molecule interacts with the surface through the lone-pair electrons, it is easy to understand why NH\textsubscript{3} prefers to M-sites in PtM surface. The lone pair electrons prefer to interact more strongly to the electron deficient M-atoms than Pt atoms which are more negatively charged due to electron transfer from the M-atoms. This is also demonstrated in the Fig.3, where we show that DOS of the lone pair on CoPt surface. The lone pair is mainly composed of N-P\textsubscript{z} orbital with little contribution from N-s orbital\textsuperscript{[14]}. From the figure it can be understood that, when the NH\textsubscript{3} molecule is adsorbed on one of the Co, it donates lone pair electrons to that Co and therefore lone-pair-DOS moves upwards in energy w.r.t the case when it is adsorbed on Pt-site. NH\textsubscript{3} molecule is therefore less nucleophilic on negatively charged Pt sites.

In conclusion, we have studied the cooperative roles of charge transfer, magnetism and strain in adsorption of NH\textsubscript{3} on FePt, CoPt and NiPt surfaces. Since NH\textsubscript{3} has a larger adsorption energy on M-sites compared to Pt sites, it is possible to achieve the selective NH\textsubscript{3} coverage of M sites on PtM surfaces. Such selective coverage is easiest in the case of FePt due to the largest M spin moments, strongest charge transfer and associated strain effects. Among the three mechanisms, the effects of charge transfer and strain are the largest, while the contribution of magnetism is relatively modest. We therefore predict FePt to be the most effective among the three. In principle, one can propose a three component descriptor \( D = D(\Delta q, \Delta m, \Delta \epsilon) \), where three components of the descriptor measure the change in charge, magnetic moment and strain effects in PtM surfaces compared to that of elemental M-surface.

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| PtM  | Lattice constants | Magnetic moments on M-site ($\mu_B$) |
|------|------------------|-----------------------------------|
|      | $a$ (Å)          | $c$ (Å)                           |
| FePt | 2.70             | 3.82                              |
|      |                  | 3.01 (2.58)                       |
| CoPt | 2.65             | 3.74                              |
|      |                  | 1.9 (1.7)                         |
| NiPt | 2.67             | 3.78                              |
|      |                  | 0.8 (0.7)                         |

Table 1: The lattice constants and magnetic moments on the M-site of M(Fe,Co,Ni)Pt in their L1$_0$. In the bracket, we also show the values of the magnetic moments for pure M-surfaces.

| Surface     | Adsorption Site | Adsorption energies (eV) |
|-------------|-----------------|--------------------------|
| Fe (110)    | Fe              | -0.72                    |
| Co (0001)   | Co              | -0.69                    |
| Ni (111)    | Ni              | -0.80                    |
| Pt (111)    | Pt              | -0.95                    |
| FePt        | Fe              | -0.85                    |
|             | Pt              | -0.53                    |
| CoPt        | Co              | -0.80                    |
|             | Pt              | -0.66                    |
| NiPt        | Ni              | -0.87                    |
|             | Pt              | -0.74                    |

Table 2: Calculated adsorption energies on ‘on top’ sites for different transition metal surfaces.

| Surface    | Site   | $n_\uparrow$ | $n_\downarrow$ | $(n_\uparrow+n_\downarrow)$ |
|------------|--------|--------------|----------------|-----------------------------|
| Pt         | Pt     | 5.00         | 5.00           | 10.00                       |
| Fe (011)   | Fe     | 5.30         | 2.71           | 8.01                        |
| Co (0001)  | Co     | 5.35         | 3.65           | 9.00                        |
| Ni (111)   | Ni     | 5.32         | 4.68           | 10.00                       |
| FePt       | Pt     | 5.45         | 5.37           | 10.82                       |
|            | Fe     | 5.32         | 1.86           | 7.18                        |
| CoPt       | Pt     | 5.41         | 3.07           | 10.48                       |
|            | Co     | 5.22         | 3.30           | 8.52                        |
| NiPt       | Pt     | 5.31         | 5.03           | 10.34                       |
|            | Ni     | 5.22         | 4.43           | 9.65                        |

Table 3: Spin resolved Bader charge per atom for different atoms on different surfaces.

| Metal  | Magnitude of the surface vector in Å |
|--------|-------------------------------------|
|        | PtM                                |
| Fe     | (2.87,2.02)                        |
| Co     | (2.50,2.50)                        |
| Ni     | (2.48,2.48)                        |

Table 4: The role of charge transfer, magnetism and strain effects in the reversal behaviour of adsorption.
Figure 1: (Color online) The density of states projected on M (Fe,Co,Ni) d-states of FePt,CoPt and NiPt.
Figure 2: (Color online) (a) The density of states of NH₃ molecule in gas phase (b) the Co-d projected DOS and NH₃ projected DOS for NH₃ adsorbed Co (0001) surface and (c) d-projected DOS for the Co(0001)
Figure 3: (Color online) The density of states projected to the lone pair of NH$_3$ molecule adsorbed on CoPt surface.
Figure 4: (Color online) NH$_3$ adsorbed on FePt surface (viewed along c-axis) as a representative of the adsorption geometry.