Cation/anion dependence of metal ammine borohydrides/chlorides studied by *ab initio* calculations

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Abstract

Ammonia (NH₃), which contains about 18 mass% of hydrogen, is regarded not only as one of the most promising hydrogen storage materials but also as an efficient carbon-free energy carrier which can be directly used by *e.g.* high-temperature solid oxide fuel cells. For the development of the NH₃-based sustainable society, it is important to improve NH₃ storage technologies. In this paper, we have studied the microscopic properties of NH₃ absorption in metal borohydrides and metal chlorides by *ab initio* calculations. We have revealed that there is a systematic cation dependence in the NH₃ absorption properties of such materials, and the properties of NH₃ absorption are mainly governed by NH₃-cation interactions and NH₃-anion repulsions.

Keywords: ammonia storage, hydrogen storage, *ab initio*, microscopic property

1. Introduction

The development of a carbon-free sustainable society is one of the most important tasks for the human beings, and the society in which energies are generated from renewable energy sources and are stored and transferred in hydrogen (H₂) is regarded the most promising answer for this task.

Ammonia (NH₃) can be regarded as one of the most promising hydrogen storage materials since it contains about 18 mass% of hydrogen atoms and can be liquefied at about 1 MPa. We can obtain H₂ molecules from NH₃ by thermal decompositions or chemical reactions. For the latter, H₂ molecules are easily obtained from MH-NH₃ system (MH: alkali metal hydride) [1, 2], and the hydrogen desorption property of this system depends on the ionicity of alkali

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metals [3, 4]. The direct use of NH_3 through *e.g.* high-temperature solid oxide fuel cell (high-temperature SOFC) is also one of the most promising systems for the renewable energy society [5].

Though the storage and transfer of pure NH_3 is easier than that of pure H_2 , pure NH_3 is a gas state at ambient conditions and also has toxicity. So it is desired to treat NH_3 more safely and more easily. We can treat NH_3 more easily with low partial pressures by ammine complexes of metal chlorides (M_nCl) or borohydrides (M_nBH_4). They can store high density of NH_3 and are promising energy carriers in the hydrogen energy society [5, 6, 7].

Magnesium chlorides MgCl_2 can store high density of NH_3 and the volumetric density of NH_3 in ammine complex $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ is up to 93% of that of liquid ammonia [8, 9]. Sørensen *et al.*[7] performed density functional theory calculations on metal ammine salts and proposed that the fast NH_3 absorption/desorption processes is explained by a mechanism in which individual chains of the ammines are released from the surface of the crystal.

Lithium borohydride (LiBH_4) absorbs NH_3 and makes $\text{Li}(\text{NH}_3)_m\text{BH}_4$ ammine complex, where $m = 1 - 4$, and can be regarded an effective NH_3 storage materials [10, 11]. Calculations on the electronic structure of $\text{LiBH}_4 \cdot \text{NH}_3$ are performed by Ramzan *et al.*[12] Magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) and Calcium borohydride ($\text{Ca}(\text{BH}_4)_2$) also can store NH_3 and have been studied as potentially promising hydrogen storage materials [6, 13].

For the development of the NH_3 -based hydrogen energy society, it is important to reveal the microscopic mechanism of NH_3 absorption in these systems. The purpose of this paper is to get insights into the cation/anion dependence of the NH_3 absorption properties of $\text{M}_n\text{Cl}/\text{M}_n\text{BH}_4$ systems by performing *ab initio* calculations. We mainly discuss about the geometric properties of the system.

2. Method

We have performed *ab initio* structure optimization calculations based on density functional theory (DFT) [18, 19, 20, 21, 22, 23, 24]. Exchange-correlation energy is treated by the generalized gradient approximation (PBE-GGA) [25] and the interaction between ions and electrons is treated by the projector augmented wave (PAW) method [26, 27], where we consider $1s$, $2s$, and $2s2p$ electrons of H, Li, and N atoms, respectively, as valence electrons. The plane wave expansion is performed by Γ point. The cut-off energy of the plane waves is 476 eV and that of the pseudocharge density is 2040 eV. The structure optimization calculation is performed by the projected velocity verlet method [28] and we regard that the system becomes to be stable when the energy change is within the calculation error during a few hundred steps. The time step for the structure optimizations is about 1 fs (40 a.u. $\simeq$ 0.968 fs).

The calculation cell is a cubic cell with the edge length of 16.0 Å. We put one M_nX_2 cluster and one or two NH_3 molecules in the cell, where M_nX_2 indicates Li_2Cl_2 , Na_2Cl_2 , K_2Cl_2 , Mg_1Cl_2 , Ca_1Cl_2 , $\text{Li}_2(\text{BH}_4)_2$, $\text{Na}_2(\text{BH}_4)_2$, $\text{K}_2(\text{BH}_4)_2$,

Figure 1: Schematic illustrations of the system for (a) $M_2X_2+2NH_3$, where M is the group 1 elements, and (b) MX_2+2NH_3 , where M is the group 2 elements.

Table 1: Absorption energy of NH_3 to M_nX_2 calculated from the difference of the total energy of $M_nX_2+mNH_3$ system and the sum of the energies of isolated M_nX_2 and NH_3 . The values for $2NH_3$ is the value averaged over two NH_3 molecules. The unit in eV.

	1 NH_3	2 NH_3
Li_2Cl_2	0.80	0.77
Na_2Cl_2	0.66	0.61
K_2Cl_2	0.52	0.53
Mg_1Cl_2	1.23	1.12
Ca_1Cl_2	1.06	0.99
$Li_2(BH_4)_2$	0.80	0.74
$Na_2(BH_4)_2$	0.67	0.63
$K_2(BH_4)_2$	0.54	0.52
$Mg_1(BH_4)_2$	1.01	0.93
$Ca_1(BH_4)_2$	0.94	0.88

$Mg(BH_4)_2$, $Ca(BH_4)_2$). These clusters correspond to a model of a disordered surface of the crystalline solid. Figure 1 is the schematic illustrations of the system in our calculations.

We have also performed molecular dynamics (MD) simulations to see the stability of the system. The MD simulations are performed under the canonical ensemble (constant-temperature constant-cellsize condition). The temperature is controled to be 300 K with Nosé thermostat [30]. We have performed MD simulations up to 2000 steps (about 2 ps) and during the simulations NH_3 stays on M in M_nX_2 cluster.

3. Results and Discussions

For each systems, NH_3 molecules absorb on metal (cation) atoms directing its N atom to metal atom. The cartesian coordinates of the stabilized systems are in supplementary material.

In table 1 we show the cation/anion dependence of the absorption energy of NH_3 to M_nX_2 . These energies are calculated from the difference between the

Table 2: Interatomic distances between metal atom and N in NH_3 . The unit is in Å.

	1 NH_3	2 NH_3	
Li_2Cl_2	2.08	2.09	2.09
Na_2Cl_2	2.40	2.41	2.41
K_2Cl_2	2.87	2.88	2.87
Mg_1Cl_2	2.16	2.18	2.18
Ca_1Cl_2	2.53	2.54	2.54
$\text{Li}_2(\text{BH}_4)_2$	2.08	2.10	2.09
$\text{Na}_2(\text{BH}_4)_2$	2.42	2.40	2.40
$\text{K}_2(\text{BH}_4)_2$	2.85	2.85	2.86
$\text{Mg}_1(\text{BH}_4)_2$	2.16	2.20	2.20
$\text{Ca}_1(\text{BH}_4)_2$	2.54	2.56	2.55

total energy of $\text{M}_n\text{X}_2+m\text{NH}_3$ system and the sum of the energies of isolated M_nX_2 and NH_3 .

This table shows that the NH_3 absorption energy decreases in order of $\text{Li} > \text{Na} > \text{K}$, and $\text{Mg} > \text{Ca}$. The NH_3 absorption energy of group 2 elements (MgX_2 , CaX_2) has higher (stronger) values than that of group 1 elements (Li_2X_2 , Na_2X_2 , K_2X_2). We can also see that the NH_3 absorption energies of metal chlorides are clearly larger than that of metal borohydrides for group 2 elements. On the other hand, the NH_3 absorption energies of metal chlorides and metal borohydrides take almost same values if the metal atoms are the same group 1 element, *i.e.*, the dependence of NH_3 absorption energies on anions is small for group 1 elements. The absorption energies of first NH_3 and second NH_3 also take similar values, though the energy slightly decreases when the number of absorbed NH_3 becomes 1 to 2.

Table 2 shows the cation/anion dependence of the interatomic distance between the metal atom and the N atom in NH_3 . There is clear cation dependence in the metal-N distance, *i.e.*, metal-N distance increases in order of $\text{Li} < \text{Na} < \text{K}$, and $\text{Mg} < \text{Ca}$. On the other hand, there is only small anion dependence in the metal-N distance. These results indicate that the metal-N interactions are mainly governed by cations, and the effect of anions on metal-N interactions is small.

Table 3 shows the metal-anion distances, where we take the position of anion as the position of Cl atom or B atom in BH_4 . That is, this table shows metal-Cl distances for metal chlorides and metal-B distances for metal borohydrides. These results also show clear cation dependence in metal-anion distance. The M-anion distance increases in order of $\text{Li} < \text{Na} < \text{K}$, and $\text{Mg} < \text{Ca}$. and the anion dependence is relatively small. However, in contrast to M-N distance, there is small but not negligible anion dependence in metal-anion distance, *i.e.*, metal-Cl distance is slightly shorter than metal-B distance for Li_2X_2 , and longer for MgX_2 and CaX_2 . For Na_2X_2 and K_2X_2 , it is not clear which metal-anion distance is longer than the other.

Table 3: Metal-Cl distances (for metal chlorides) and metal-B distances (for metal borohydrides). The unit is in Å.

	1NH ₃				2NH ₃			
Li ₂ Cl ₂	2.22	2.22	2.30	2.32	2.30	2.28	2.30	2.28
Na ₂ Cl ₂	2.52	2.53	2.58	2.67	2.56	2.66	2.56	2.65
K ₂ Cl ₂	2.93	2.91	3.04	2.96	3.04	2.94	3.04	2.95
Mg ₁ Cl ₂	2.23		2.23		2.28		2.28	
Ca ₁ Cl ₂	2.54		2.53		2.58		2.58	
Li ₂ (BH ₄) ₂	2.26	2.19	2.38	2.40	2.37	2.33	2.32	2.37
Na ₂ (BH ₄) ₂	2.61	2.47	2.55	2.70	2.51	2.74	2.74	2.51
K ₂ (BH ₄) ₂	2.89	2.90	3.17	2.93	2.90	3.11	2.91	3.12
Mg ₁ (BH ₄) ₂	2.15		2.26		2.23		2.24	
Ca ₁ (BH ₄) ₂	2.49		2.49		2.52		2.52	

Table 4: Nearest H_{inNH3}-Cl distances (for metal chlorides) and nearest H_{inNH3}-H_{inBH4} distances (for metal borohydrides). The unit is Å.

	1NH ₃	2NH ₃	
Li ₂ Cl ₂	3.41	3.28	3.63
Na ₂ Cl ₂	2.57	2.53	2.58
K ₂ Cl ₂	2.40	2.45	2.45
Mg ₁ Cl ₂	3.28	3.18	3.10
Ca ₁ Cl ₂	3.03	2.70	2.74
Li ₂ (BH ₄) ₂	3.02	2.96	2.89
Na ₂ (BH ₄) ₂	3.48	2.02	2.03
K ₂ (BH ₄) ₂	1.95	1.91	1.87
Mg ₁ (BH ₄) ₂	2.38	2.61	2.63
Ca ₁ (BH ₄) ₂	2.93	2.87	2.96

Table 5: Nearest (left) and farthest (right) N-H distances in NH_3 . The unit is Å.

	1NH_3		2NH_3	
Li_2Cl_2	1.037	1.039	1.037	1.039
Na_2Cl_2	1.037	1.045	1.037	1.046
K_2Cl_2	1.037	1.049	1.037	1.048
Mg_1Cl_2	1.039	1.039	1.037	1.039
Ca_1Cl_2	1.038	1.041	1.037	1.044
$\text{Li}_2(\text{BH}_4)_2$	1.037	1.039	1.037	1.039
$\text{Na}_2(\text{BH}_4)_2$	1.038	1.038	1.037	1.046
$\text{K}_2(\text{BH}_4)_2$	1.037	1.047	1.037	1.048
$\text{Mg}_1(\text{BH}_4)_2$	1.038	1.039	1.037	1.039
$\text{Ca}_1(\text{BH}_4)_2$	1.038	1.039	1.037	1.038

Table 4 shows nearest $\text{H}_{\text{inNH}_3}\text{-Cl}$ distances (for metal chlorides) and nearest $\text{H}_{\text{inNH}_3}\text{-H}_{\text{inBH}_4}$ distances (for metal borohydrides). For the systems with two NH_3 , the distances take small value when the metals are Na or K, though the $\text{H}_{\text{inNH}_3}\text{-H}_{\text{inBH}_4}$ distance for $\text{Na}_2(\text{BH}_4)_2$ and one NH_3 system is not small. For the other metal cations, on the other hand, the H atom is not close to the anions compared with that for Na_2X_2 or K_2X_2 .

It indicates that metal atom and N atom strongly interacts for Li_2X_2 , MgX_2 and CaX_2 , and coulomb interactions between $\text{H}^{\delta+}$ in NH_3 and $\text{Cl}^-/\text{BH}_4^-$ has relatively small effects on the atomic configurations.

The results of our calculations show that, although the NH_3 absorptions on metal chlorides/borohydrides are mainly governed by the metal-N interaction, anion has almost no effect on the metal- NH_3 interactions. It means that the anion dependence of these systems are directly governed by anion- NH_3 interactions and anion-metal interactions, and we can see almost no indirect effects of anion on metal-N distance.

This means that the anion dependence of the system mainly come from anion- NH_3 repulsion. For MgX_2 and CaX_2 , in which we can see clear anion dependence in the absorption energy, anion-metal-anion cluster takes bent form. Since the isolated MX_2 takes one-dimensional form, the bent structure of these cluster with NH_3 comes from the repulsion between anions and NH_3 .

In table 5 we show the cation/anion dependence of the nearest N-H distance and farthest N-H distance in NH_3 . While the nearest N-H distance takes almost same values, the farthest N-H distance depends on the cations. The farthest N-H distance takes large value when the system is Na_2X_2 or K_2X_2 , except the system $\text{Na}_2(\text{BH}_4)_2$ with one NH_3 .

As we have seen in table 4, $\text{H}^{\delta+}$ in NH_3 and Cl^- or $\text{H}^{\delta-}$ in BH_4 come close to each other for Na_2X_2 and K_2X_2 .

However, though the H-H or H-Cl distance is small for Na_2X_2 or K_2X_2 , there is almost no anion dependence in the absorption energy for group 1 elements. These results show that the effect of $\text{H}^{\delta+}\text{-H}^{\delta-}$ and $\text{H}^{\delta+}\text{-Cl}^-$ coulombic

attractions is small compared with M-N interactions, and the anion dependence of the system comes from the interaction between whole-NH₃ and whole-BH₄ or Cl, not from the specific interaction between H^{δ+} in NH₃ and H^{δ-} in BH₄ or Cl⁻.

4. Summary

We have performed *ab initio* calculations on the NH₃ absorption on Li₂Cl₂, Na₂Cl₂, K₂Cl₂, MgCl₂, CaCl₂, Li₂(BH₄)₂, Na₂(BH₄)₂, K₂(BH₄)₂, Mg(BH₄)₂ and Ca(BH₄)₂ clusters.

NH₃ absorbs on M_nX₂ directing its N atom to metal (cation) atom, and absorptions energy of NH₃ mainly depends on metal atoms and also depends on anions.

The absorption energy of NH₃ has relatively strong anion dependence for group 2 elements (MgX₂ and CaX₂), though the coulombic interaction between anion and NH₃ seems stronger for Na₂X₂ and K₂X₂. On the other hand, the structure of MX₂, where M is group 2 element, are bent by NH₃ absorption. From these results we can say that the anion dependence mainly comes from NH₃-anion repulsive interactions.

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