

ADSORPTION OF AN NH₃ MOLECULE ON THE Fe(111) SURFACE ALLOYED WITH 5% CHROMIUM

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INTISARI

Telah dilakukan penelitian mempelajari adsorpsi NH₃ pada permukaan aliansi besi-krom (111) menggunakan program QCMP 116, yang dijalankan dengan IBM PC compatible (Pentium III). Permukaan ini terdiri dari 20 atom dengan tiga lapisan, dan salah satu atom besi (pada lapisan pertama, atom No 1) diganti dengan atom krom. Molekul NH₃ yang mendatangi permukaan logam dengan arah jatuh sejajar dan tegak lurus permukaan pada beberapa posisi jatuh, dioptimasi tiga dimensi dengan program itu. Dari perhitungan BE(NH₃) dan jarak antar atom pada kondisi optimal memperlihatkan bahwa molekul NH₃ yang mendatangi permukaan dengan arah horizontal pada permukaan, atom N diarahkan pada *surface site*, salah satu ikatan N-H paralel terhadap ikatan Fe-Fe, diadsorpsi kimia secara molekular dengan rentang BE(NH₃) antara 1.2000-1.2005 eV/molekul (bila N diikat oleh Cr), 1.6010-1.9670 eV/molekul (bila N diikat ke Fe) dan 1.8909-2.2005 eV/molekul (bila N dan H diikat oleh Fe). Dan yang diarahkan pada titik tengah antara dua atom pada *edge site* diuraikan oleh permukaan. Molekul NH₃ yang mendatangi permukaan dengan arah tegak lurus permukaan, dengan atom N dan salah satu ikatan N-Hnya tegak lurus pada permukaan pada *surface site* dan *edge site* diserap secara fisika dengan rentang BE(NH₃) antara 0.1543-0.6267 eV/molekul.

ABSTRACT

QCMP 116 program, runs on IBM PC compatible (Pentium III) had been used to study interactions an NH₃ molecule on iron-chromium (111) alloy surface. This surface consisted of 20 atoms with three layers, and one iron (in the first layer, No 1) was substituted by chromium. An oncoming NH₃ (with the planar molecular plane parallel or perpendicular to surface), at many positions, was optimized three dimensionally by that program. Observing the Binding Energy of an NH₃ on surface (BE(NH₃)) and its interatomic distances at the optimized conditions showed that: an oncoming NH₃ molecule, with molecular plane parallel to the surface, N atom was oriented to the surface site, one of its N-H bond parallel to the Fe-Fe bond, was chemisorbed molecularly with BE(NH₃) in range 1.2000 – 1.2005 eV/molecule (when N was bonded to Cr), 1.6010 - 1.9670 eV/molecule (when N was bonded to Fe) and 1.8909 – 2.2005 eV/molecule (when N and H were bonded to Fe). And that, was oriented to the middle point between two atoms at the edge site was chemisorbed atomically. However, an oncoming NH₃ with molecular plane perpendicular to the surface, with N atom and one of its N-H bond perpendicular to the surface either on surface site or edge site were adsorbed physically with BE(NH₃) in the range of 0.1543 – 0.6267 eV/molecule.

Keywords: Adsorption, Binding Energy

INTRODUCTION

Catalyst plays an important role in the ammonia synthesis from N₂ and H₂ gases. Iron has been used as a catalyst in industry of ammonia. Its yield is about 20%. Many investigations has been done to increase this product. Norskov and Stoltze¹ reported that N₂ was adsorbed

atomically to iron surface, followed by reaction with H₂ gas produced the adsorbed ammonia and then desorption of ammonia. The activity of iron catalyst depends strongly on structure of iron surface. The Fe(111) surface is highly active, about 25 times as active as the Fe(100) surface and about 400 times more active than the Fe(110) surface at 200 atm and 525°C.²

Dowben, et al.,³ found that N_2 was adsorbed molecularly and atomically to Cr(110) surface. Kusuma⁶ also found that N_2 was adsorbed atomically on Fe(111), Fe/Cr(111) (alloy Fe-Cr), and Cr(111). Since crystal structure of iron and chromium are BCC with lattice parameter (a_0) are 2.87 and 2.88 Å, respectively, we try to alloy the Fe(111) surface with Cr atom.

The aim of this investigation was to study the effect of the alloyed Fe (5% Cr) to the BE(NH_3) on the Fe (111) surface. The surface to be used in these calculations consists of 20 atoms. There are ten atoms on the first layer, five atoms on the second and on the third layer (Figure 1). Then, the iron atom No 1 was substituted by chromium and it was defined as $Fe_{19}Cr$ (111).

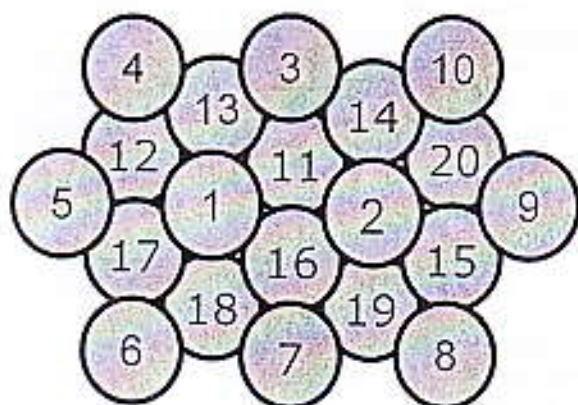


Figure 1: $Fe_{19}Cr$ (111) surface; 1: Cr atom; 2-20: Fe atom; 1-10: first layer atoms; 13-17: second layer atoms; 11, 12, 18-20: third layer atoms

An NH_3 with molecular plane parallel (NH_3 parallel) and perpendicular (NH_3 perpendicular) to the surface came to surface, at

many positions. The process that happened for adsorption was investigated by three dimensional (3D) optimization on QCMP 116 programs, runs on IBM PC compatible (Pentium III), with accuracy 0.00001 eV. In this calculations, a NH_3 molecule was assumed to be planar with $rN-H = 0.992$ Å and $\angle HNH = 120^\circ$ (D_{3h}).

METHODOLOGY

Formerly EHMO method worked on mainframe. In order to get more applications, this program was modified as ASSED program (works on surface chemistry), and Calzaferri program (adopted for studying inorganic compound).⁵ In this investigation, the calzaferri program was used to study the interaction of gases on a surface. For that purpose, some of its atomic parameters needed to be modified.

The inputs of this program are number of atoms, coordinate of each atoms and atomic parameters of those atoms. The atomic parameters are: the valence electrons of those atoms, types of orbital occupied by those valence electrons and their respective orbital energies (in eV) and orbital exponents (in a.u). For valence electron occupies a suborbital d , there are two types of orbital exponents (ξ_1 and ξ_2), and two types orbital exponent coefficients (C_1 and C_2). Parameters used in these calculations are listed in Table 1. Parameters for N atom were taken from the program. While those for Fe, Cr, N, and H were modified by Kusuma.⁶ The coordinate used in this calculations was internal coordinate.

Table 1: The parameters used in the present calculations

Atom	ns	ξ_s	VSIE (eV)	np	ξ_p	VSIE (eV)	nd	ξ_1	VSIE (eV)	ξ_2	C_1	C_2
Cr	4	1.600	-6.77	4	1.30	-3.72	3	4.95	-9.50	1.60	0.4878	0.7205
Fe	4	1.700	-8.75	4	1.40	-5.70	3	5.35	-10.5	1.80	0.5369	0.6678
N	2	2.140	-26.0	2	1.95	-13.4						
H	1	1.300	-12.6									

VSIE = Valence State Ionization Energy

Outputs of this program are the total energy of system (E_T in eV), and distance matrices that give information about interatomic distance (d),

overlap population matrices that reflect the strength of interatomic bond, etc. Detail about

the program is written in the manual of the program.⁵

The surface to be studied was shown in Figure 1. The N atom of NH_3 parallel was oriented to atoms on the surface with one of its N-H bond parallel to the line connected atom *i* and *j* as *i-j*. Those were atom No 1, 2 (in the surface site), atom No 5, 7, 8, 9 (in the edge site), No 13, 16, 17 (in the second layer), No 11, 12, 18 (in the third layer). It also had been oriented to the middle point of atom *i* and *j*, as $\frac{1}{2}(i-j)$. Those were $\frac{1}{2}(1-2)$, $\frac{1}{2}(7-8)$, $\frac{1}{2}(16-17)$, $\frac{1}{2}(7-8)$, $\frac{1}{2}(8-9)$, $\frac{1}{2}(1-5)$, $\frac{1}{2}(2-9)$, $\frac{1}{2}(1-7)$ and $\frac{1}{2}(1-16')$, 16' was the projection of atom No 16 to the surface. The initial dM-N (M= Fe, Cr) for the surface and edge site was 1.50Å, while that for the second and third layer and $\frac{1}{2}(i-j)$ was 1.00 Å. On the other hand the N atom of NH_3 perpendicular with one of its N-H perpendicular to the surface was oriented to atom No 1, 2, 9, $\frac{1}{2}(8-9)$ and $\frac{1}{2}(1-2)$ (with dM-N initial 1.50Å).

During optimization (manual) surface was assumed to be rigid. Optimization begin with N atom followed by H atoms simultaneously (C_{3v}). At the beginning of each set of optimization the increment/decrement of the vector length was assumed to be 0.100 Å, while for bond angle and dihedral angle were 2.0°. When we get close to the optimized condition, these values were change to 0.001 Å and 0.050°, respectively. In some cases to keep the NH_3 molecule not leave the surface immediately, we defined that at the first step of optimization, the length of vector N should not be greater than 2.20 Å.

In this experiment, *d* and $\text{BE}(\text{NH}_3)$ in optimal condition were used to predict whether an NH_3 molecule was adsorbed physically or chemically to surface. $\text{BE}(\text{NH}_3)$ was calculated by:

$$\text{BE}(\text{NH}_3) = E_{\text{r}}(\text{surface}) + E_{\text{r}}(\text{NH}_3) - E_{\text{r}}(\text{surface} + \text{NH}_3)$$

$\text{BE}(\text{NH}_3)$ would reflect the strength of surface to adsorb the NH_3 molecule, indirectly the possibility of surface to desorb the adsorbed NH_3 .

RESULTS AND DISCUSSIONS

We assumed that bond was broken if *d* was longer than 2.3 Å. Physical adsorption occurred when *d* 2.2 – 2.3 Å and $\text{BE}(\text{NH}_3)$ about 1.0 eV/molecule. Those values for chemically adsorption were less than 2.2 Å and greater than 1.0 eV/molecule. Chemically adsorption was divided into molecularly and atomically chemically adsorption.

Results of these calculations showed that an oncoming NH_3 parallel to the surface usually was chemisorbed molecularly. When N was bonded to the substituted metal, Cr, $\text{BE}(\text{NH}_3)$ was about 1.2000-1.2005 eV/molecule and 1.8729–1.8746 Å, respectively (Table 2, No 1-7). These for $\text{Cr}_{20}(111)$ were 0.9797-1.1600 eV/molecule and 1.8909 – 1.9180 Å, respectively⁶ (Tabel 3). The structure of the adsorbed NH_3 was shown on Figure 2(a), with N on-top of Cr atom and all H atoms had been pointed out of surface. Structure (a) also observed when N atom was bonded to Fe atom (Tabel 2, No 8-10), with its dFe-N, $\text{BE}(\text{NH}_3)$ were in ranges of 1.6390-1.7000 Å and 1.6010-1.9670 eV/molecule, respectively. These for $\text{Fe}_{20}(111)$ were 1.5220-1.6385 Å and 2.0079-2.1076 eV/molecule, respectively (Tabel 3). Thus 5% Cr on Fe(111) decrease $\text{BE}(\text{NH}_3)$ of $\text{Fe}_{20}(111)$ if the adsorbed NH_3 had structure (a), by increasing the dFe-N.

Structure (b) (Figure 2) occurred when an NH_3 molecule (parallel) was oriented to $\frac{1}{2}(1-2)$ and one of its N-H bond was parallel (1-2) (Tabel 2, No 15). In this case both N and H atoms were bonded to the same surface site (Fe atom). This structure was also found when NH_3 parallel came to atom on the third layer (Tabel 2, No 14). This structure (b) had $\text{BE}(\text{NH}_3)$ around 1.90 eV/molecule (only two data were available). Efendy⁷ work with $\text{Fe}_{20}(111)$ point out that this $\text{BE}(\text{NH}_3)$ was in ranges 1.9380-2.0138 eV/molecule (>1.90 eV/molecule). Banon⁸ worked with $\text{Cr}_{20}(111)$ did not observed this structure (b) (Tabel 3).

Structure (c) (Figure 2) with both N and H atoms were adsorbed by different surface sites (Fe atom) had $\text{BE}(\text{NH}_3)$ in the ranges of 2.1201- 2.2000 eV/molecule. This value for $\text{Cr}_{20}(111)$ was 1.1616-1.3440 eV/molecule and for $\text{Fe}_{20}(111)$ was around 2.20 eV/molecule (Tabel 3, only two data were available).

Table 2: BE(NH₃) and internuclear distances of an oncoming NH₃ with molecular plane parallel and perpendicular to the surface, at many positions.

No	Oncoming Position	Total Energy	d Cr-N	d Fe-N	d Cr-H	d Fe-H	d N-H	d H-H
1	//, 17, 18'-1	1.8729 (1)	*	*	*	1.0050	1.6151	1.2005
2	//, ½(1-16), 18'-1	1.8729 (1)	*	*	*	1.0050	1.6151	1.2005
3	//, 16, 1-18'	1.8733 (1)	*	*	*	1.0050	1.6151	1.2005
4	//, 13, 18'-1	1.8737 (1)	*	*	*	1.0050	1.6151	1.2005
5	//, ½(16-17), 1-18'	1.8740 (1)	*	*	*	1.0050	1.6151	1.2005
6	//, 1, 1-2	1.8740 (1)	*	*	*	1.0050	1.6154	1.2000
7	//, 16, 18'-1	1.8746 (1)	*	*	*	1.0050	1.6151	1.2004
8	//, 2, 1-2	*	1.5390 (2)	*	*	1.0300	1.5945	1.9670
9	//, 9, 1-2	*	1.7000 (9)	*	*	1.0260	1.5952	1.6010
10	//, 12, 18'-1	*	1.6863 (4)	*	*	1.0280	1.5969	1.6262
11	//, 8, 2-1	*	1.5410 (8)	*	1.7948 (7)	1.1150	1.6151	2.1201
12	//, 5, 2-1	*	1.5150 (5)	*	1.7707 (4)	1.1440	1.6300	2.1625
13	//, 7, 2-1	*	1.5230 (7)	*	1.7594 (6)	1.1400	1.6253	2.2005
14	//, 11, 18'-1	*	1.4869 (3)	*	1.4436 (3)	1.0870	1.6908	1.9708
15	//, ½(1-2), 1-2	*	1.5395 (2)	*	1.6502 (2)	1.0490	1.6400	1.8909
16	⊥, ½(1-2), ½(1-2)	2.2123 (1)	*	2.4186 (1)	*	0.9850	1.7161	0.6267
17	⊥, 2, 2	2.2164 (1)	*	2.2305 (1)	*	0.9850	1.7061	0.5830
18	⊥, 1, 1	*	*	2.3275 (1)	*	0.9870	1.7095	0.2935
19	⊥, 9, 9	*	*	*	1.8859 (9)	0.9920	1.7182	0.1543
20	⊥, ½(8-9), ½(8-9)							N-H bond was broken
21	//, ½(7-8), 1-2							N-H bond was broken
22	//, ½(8-9), 2-1							N-H bond was broken
23	//, ½(8-9), 1-2							N-H bond was broken
24	//, ½(1-7), 1-2							N-H bond was broken
25	//, ½(1-5), 1-2							N-H bond was broken
26	//, ½(2-9), 1-2							N-H bond was broken
27	//, 18, 1-18'							N-H bond was broken

// and ⊥; mean the oncoming NH₃ with molecular plane parallel and perpendicular to surface, respectively.

1, 1-2; an N atom on-top atom No 1 and an N-H parallel to 1-2 line

½(1-2); an N atom on-top in the middle of atom No 1 and 2

1.8729(1); the internuclear distance of N atom to atom No 1 is 1.8729Å

* d > 2.3 Å

Table 3: Binding Energies and internuclear distances of an NH₃ molecule chemisorbed on some surfaces.

surface	BE(NH ₃) in eV/molecule in structure			dM-N in Å in structure		
	a	b	c	a	b	c
Fe ₂₀ (111) ^a	2.0079-2.1076	1.9380-2.0138	2.1076-2.2133 [*]	1.6385-1.5220	1.4916-1.5693	1.5220-1.5280
Fe ₁₉ Cr(111)	1.2000-1.2005 [*]	-	-	1.8729-1.8745	-	-
Cr ₂₀ (111) ^a	1.8010-1.9570 ^{**}	1.8909-1.9708 [*]	2.1201-2.0005	1.6350-1.7002	1.4869-1.5335	1.5150-1.5410
Cr ₁₉ (111) ^a	0.9797-1.1600	-	1.1616-1.3440	1.8909-1.9180	-	1.7360-1.8909

^a N bonded to Cr atom

^{**} N bonded to Fe atom

^{*} two data were available

In conclusions, for N bonded to Cr atom, 5% Cr decreased the $BE(NH_3)$ Fe(111) sharply for N bonded to Fe atom, 5% Cr reduced the probability structure (b) to be formed on Fe(111). In the same time structure (c) (more common on Cr(111)) was introduced. Unfortunately, the $BE(NH_3)$ about the same as Fe(111).

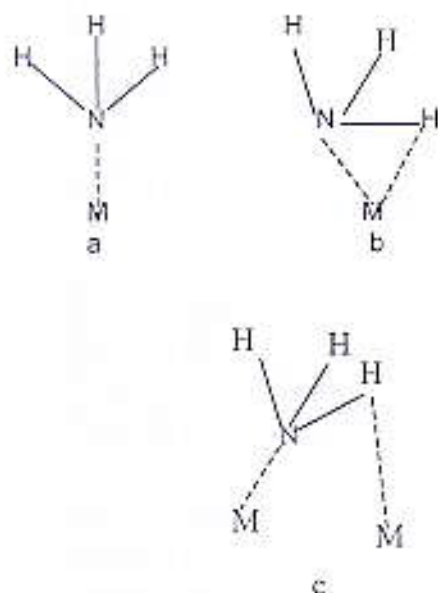


Figure 2: Suppose structures for the adsorption of ammonia to the atom, M was Cr or Fe atom.

When N atom of NH_3 parallel was oriented to $\frac{1}{2}(i-j)$ with i and j were atoms in edge site (Table 2, No 21-26) and to the third layer (Table 2, No 27), with one of its N-H bond parallel to the i-j line, the NH_3 was chemisorbed atomically. The N-H bond was broken, N and H atoms were bonded to irons at different location. As a result, its BE increased very fast.

Generally, the NH_3 perpendicular was adsorbed physically. In the surface site N atom would go to Cr atom and $d(N-H)$ was shorter than that of free NH_3 molecule (Table 2, No 16-18). At the edge site, H atom would go to Fe atom and $dN-H$ was equal to of free NH_3 (Table 2, No 19, with $dCr-H = 1.8859 \text{ \AA}$). As a whole, their $BE(NH_3)$ were less than those chemisorbed

molecularly. The same results were observed on $Cr_{20}(111)^6$ and on $Fe_{20}(111)^7$.

CONCLUSIONS

$Fe_{10}Cr(111)$ surface might decrease $BE(NH_3)$, when N was bonded to the substituted Cr atom. When N bonded to the Fe atom, its $BE(NH_3)$ was comparable with $Fe_{20}(111)$. This was due to the substituted Cr changed the chemical properties of some edge position of $Fe_{20}(111)$. It was assumed, increasing the percentage of Cr on Fe(111) would decrease the $BE(NH_3)$ value. However, these results would not be guaranteed that high doping Fe be a good catalyst compared with pure Fe surface.

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