ADSORPTION OF AN NH$_3$ MOLECULE ON Cr(111) SURFACE BY QCMP 116 PROGRAM

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ABSTRACT

Interactions of an NH$_3$ molecule on chromium (111) surface consists of 20 atoms with three layers has been studied by QCMP 116 (Calzaferri) program, run on IBM PC compatible (Pentium III, 660 MHz). An oncoming NH$_3$ (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 NH$_3$ on surface (BE (NH$_3$)) and inter atomic distances at the optimized conditions. It's showed that: an oncoming NH$_3$ molecule, with molecular plane parallel to the surface, N atom was oriented to atoms of the first and third layer. One of its NH bond was parallel to the Cr–Cr bond were chemisorbed molecularly with BE(NH$_3$) in range of 0.9797-1.3421 eV/molecule. On the second layer was chemisorbed atomically. However, an oncoming NH$_3$ with molecular plane perpendicular to the surface (with N atom and one of its N–H bond perpendicular to Cr atom) was adsorbed physically with BE(NH$_3$) in a range of 0.4903-0.5614 eV/molecule.

INTRODUCTION

Catalyst plays an important role in the ammonia synthesis from N$_2$ and H$_2$ gases. Iron has been used as a catalyst in an industry of ammonia with an yield of 20%. Many investigations had been done to increase this yield. Norskov and Stoltze [1] reported that N$_2$ was adsorbed atomically to iron surface, followed by reaction to H$_2$ 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 and 400 times as active as the Fe(100) and Fe(110) surface, at 200 atm and 525 °C [2], respectively. Dowben *et al.* [3] found that N$_2$ was adsorbed molecularly and atomically on Cr (110) surface. This is not surprising, since both Fe and Cr have the same crystal structure e.i *bcc* with a$_o$ (lattice parameter) 2.78 and 2.88 Å, respectively. Kusuma [4] also found that N$_2$ was adsorbed atomically on Fe (111), Fe/Cr(111) (alloy Fe-Cr), and Cr(111).

The aim of this investigation is to study the BE(NH$_3$) on the Cr(111) surface. It was defined that the binding energy of NH$_3$ on the surface as (BE(NH$_3$)). The surface to be used in these calculations consists of 20 atoms. 10 atoms on the first layer, five atoms on the second and on the third layer (Fig. 1). Then an NH$_3$ with molecular plane parallel (NH$_3$ parallel) and perpendicular (NH$_3$ perpendicular) to surface, at many positions, comes to the surface. The process that happened for adsorption was investigated by three dimensional (3D) optimization on QCMP 116 program, run on IBM PC compatible (Pentium III), with accuracy 0.00001 eV. In

this calculations, an NH$_3$ molecule was assumed to be planar with d(N-H) = 0.992 Å, and $\angle$ HNH = 120° (D$_{3h}$).

EXPERIMENTAL SECTION

Materials and Instrumentation

This experiment is Cr (111) surface consists of 20 atoms with three layers. An oncoming NH$_3$ (with the planar molecular plane parallel or perpendicular to surface) has been studied by QCMP 116 (Calzaferri) program, run on IBM PC compatible (Pentium III, 660 MHz).

Procedure

Formerly EHMO method worked on mainframe. In order to get more applications, this program was modified as ASED program (work on surface chemistry), and QCMP 116 program (adopted for studying inorganic compound) [5]. In this investigation, the QCMP 116 program was used to study the interaction of gases on a surface. For that propose, some of its atomic parameters were modified.

The inputs of this program are number of atoms, coordinate of each atom and atomic parameters of those atoms. The parameters including: valence electrons of those atoms, type of orbital occupied by those valence electrons and their respective orbital energies (in eV) and orbital exponents (ξ in a.u). For valence electron occupies a sub orbital d, there are two types of orbital exponent (ξ_1 and ξ_2), and two types of

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Table 1. The parameter used in the present calculations

Atom	ns	ξs	VSIE (eV)	np	ξp	VSIE (eV)	nd	$\xi 1$	VSIE (eV)	$\xi 2$	C1	C2
Cr	4	1.600	-6.77	4	1.30	-3.72	3	4.95	-9.50	1.60	0.4876	0.7205
N	2	2.140	-26.0	2	1.95	-13.4						
H	1	1.300	-12.6									

VSIE = Valence State Ionization Energy
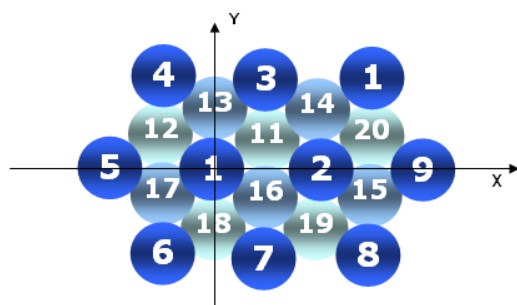
Fig 1. Cr(111) surface, 1-10: first layer; 13-17: second layer; 11, 12, 18-20: third layer

coefficient orbital exponent (C_1 and C_2). Parameters used in these calculations were listed in Table 1. Parameters for N atom were taken from the program while for Cr and H was modified by Kusuma [6]. The coordinate to be used in these calculations was internal coordinate.

Outputs of this program are the total energy of system (E_T in eV), and distance matrices that give information about inter atomic distance (d in Å), overlap population matrices, that reflect the strength of inter atomic bond, etc. Detail about the program is written in the manual of the program (Calzaferri and Brandle) [5].

The surface to be studied was shown in Fig. 1. The N atom of the NH_3 parallel was oriented to atoms of the surface and one of its N–H bond was parallel to the Cr–Cr bond. Those were atoms No 1, 2 (in the surface site); No 3, 7, 8, 9 (in the edge site) both with d(Cr-N) initial = 1.5 Å; No 13, 16 (in second layer), No 11, 18 (in third layer) both with d(Cr-N) initial = 1.0 Å. It also had been oriented to the middle point between two atoms with d(Cr-N) initial = 1.0 Å. Those were between atom No 1 and 2, atom No 1 and 5, atom No 1 and 7, atom No 7 and 8, atom No 8 and 9, atom No 16 and 17, and atom No 1 and 16' (16' was the projection of atom No 16 to the surface). On the other hand the N atom and one of N–H bond of the NH_3 perpendicular was oriented to atom No 1, 7, 9, and between atom No 1 and 2 (with d(Cr-N) initial = 1.0 Å). During 3D optimization (manual) surface was assumed to be rigid. Optimization had begun with N atom followed by H atoms simultaneously. At the beginning, for each set of optimation the increment/decrement of the vector length was assumed to be 0.1 Å, while for bond angle and dihedral angle were 2°. When we got close to the optimized condition,

those values were changed to 0.001 Å and 0.05°, respectively. In same cases, to keep the NH_3 molecule not to leave the surface immediately, we defined that at the first step of optimation the length of vector N should not be greater than 2.200Å.

In this experiment, (d) and BE(NH_3) in optimal condition were used to predict whether an NH_3 molecule was adsorbed physically or chemically to surface. This was due to BE(NH_3) reflected strength of surface to adsorb the NH_3 molecule, indirectly the possibility of a surface to desorbed the adsorbed NH_3. BE(NH_3) was calculated by:

$$BE(NH_3) = E_T (surface) + E_T (NH_3) - E_T (surface + NH_3)$$

RESULT AND DISCUSSION

Table 2 showed the results of these calculations. An NH_3 parallel usually was chemisorbed molecularly with BE(NH_3) and d(Cr-N) in the ranges of 0.9797-1.3440 eV/molecule and 1.7360-1.9180 Å, respectively. For Fe(111) surface (with similar structure) those values were in the ranges of 1.9380-2.2130 eV/molecule and 1.4920-1.6390 Å [7], respectively. It might be Cr(111) desorbed the adsorbed NH_3 better than Fe(111) surface.

There were two types of bonding structure of NH_3 parallel on Cr(111) surface, a and b (Fig. 2). Structure b had BE(NH_3) greater than a, since two atoms of the NH_3 molecule were bonded to the different Cr atom of the surface. Structure b was predominantly found when the NH_3 parallel was oriented to the edge of surface (Table 2. No 1, 4, 5, 7). The edge position was reactive. Some of edge positions also adsorbed NH_3 with structure a with BE(NH_3) less than of and d(Cr-N) greater than of structure b (Table 2. No 14, 15). Thus, edge positions were comparable with site positions (Table 2. No 10, 11 Vs 14, 15).

When N atom of NH_3 parallel was oriented to atom in second layer it would be chemisorbed atomically. The N-H bond was broken; N and H atoms were bonded to different atoms on surface. In this case the d(N-H) was greater than 2.3 Å. As a result the calculated binding energy was not the BE(NH_3) (Table 2, No 20 and 21). The same results were observed when an NH_3 molecule came to the edge site (Table 2. No 23, 24). On the contrary when NH_3 parallel was oriented to atoms in the third layer, this was adsorbed

Table 2. BE(NH$_3$) and internuclear distances of An NH$_3$ oncoming with molecular plane parallel and perpendicular to the Cr(111) surface at many positions.

No	P o s i s i	d Cr-N (Å)	d Cr-H (Å)	d N-H (Å)	d H-H (Å)	BE(eV)
1 //	9, 1-2	1.7360 (9)	1.8283 (10)	1.0590	1.6043	1.3421
2 //	½(1-5), 2-1	1.7382 (5)	1.8358 (4)	1.0580	1.6020	1.3440
3 //	18, 1-18'	1.7586 (7)	1.8745 (6)	1.0440	1.6039	1.1663
4 //	7, 1-2	1.7630 (7)	1.8688 (8)	1.0430	1.6053	1.1616
5 //	7, 2-1	1.7640 (7)	1.8706 (6)	1.0420	1.6052	1.1616
6 //	½(1-7), 1-7	1.7652 (7)	1.8825 (6)	1.0420	1.6038	1.1665
7 //	8, 1-2	1.8260 (8)	1.9198 (7)	1.0270	1.6035	1.2078
8 //	11, 11'-1	1.8909 (1)	-	1.0050	1.6134	1.0216
9 //	½(1-7), 1-2	1.8920 (7)	-	1.0050	1.6134	1.0215
10 //	½(1-2), 1-2	1.8928 (2)	-	1.0050	1.6134	1.0218
11 //	1, 1-2	1.8930 (1)	-	1.0050	1.6134	1.0192
12 //	½(1-16),1-16'	1.8930 (1)	-	1.0050	1.6134	1.0216
13 //	½(16-17),1-18'	1.8932 (1)	-	1.0050	1.6134	1.0216
14 //	3, 1-2	1.9070 (3)	-	1.0060	1.6133	1.1600
15 //	½(8-9), 1-2	1.9180 (8)	-	1.0042	1.6141	0.9797
16 ⊥	½ (1-2), NH→1'	2.2901 (1)	-	0.9850	1.7060	0.4903
17 ⊥	9, NH →9	2.2979 (10)	-	0.9860	1.7078	0.5614
18 ⊥	1, NH →1	2.3142 (2)	-	0.9850	1.7061	0.4668
19 ⊥	7, NH →7	2.3202 (8)	-	0.9850	1.7061	0.5523
20 //	13, 1-13'	N – H Bond was broken				
21 //	16, 1-16'	N – H Bond was broken				
22 //	¾ (16), 1-16'	N – H Bond was broken				
23 //	½ (7-8), 1-2	N – H Bond was broken				
24 //	½ (7-8), 2-1	N – H Bond was broken				

//; means an oncoming NH$_3$ with molecular plane parallel to surface
1,1-2; an N atom on-top atom No 1 and an N-H bond parallel to 1-2 line
 ½(1-2); an N atom on-top in the middle atom No 1 and 2
⊥; an oncoming NH$_3$ with molecular plane perpendicular to surface
 2.3202 (8); the internucler distance of N atom to atom No 8 is 2.3202 Å
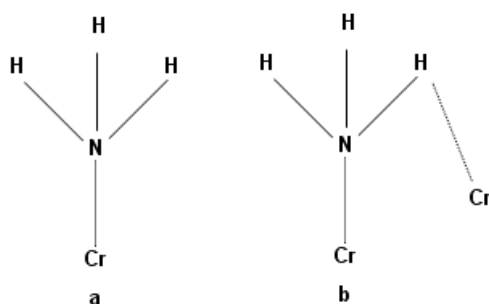
Fig 2. Suppose structures for the adsorption of ammonia to the Chromium metal

molecularly (No 3, with structure b, No 8 with structure a)

Sometimes (not often) structure b was also observed on Fe(111), when an NH$_3$ parallel came to the edge site. Usually the probability to get structure a >>> b for Fe(111) [7].

Generally, the NH$_3$ perpendicular was adsorbed physically (Table 2, No 16-19) with BE(NH$_3$) an d(Cr-N) in the ranges of 0.4903-0.5614 eV/molecule and 2.2901–2.3202 Å, respectively. Their BE(NH$_3$) was less than BE(NH$_3$) that chemisorbed molecularly and d(N-H) around 2.3 Å. The same results were observed for Fe(111) surface [7].

CONCLUSION

Structure b had BE(NH$_3$) greater than a, since two atoms of the NH$_3$ molecule were bonded to the different Cr atom of the surface. More structure b was observed on edge site than edge position. It was assumed that Cr(111) surface might desorbs ammonia molecule better than Fe(111), since BE(NH$_3$) for Cr(111) was less than Fe(111).

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