

ADSORPTION OF AN NH₃ MOLECULE ON THE Cr(111) SURFACE By QCMP 116 PROGRAM

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INTISARI

Studi interaksi molekul NH₃ pada permukaan Cr(111) menggunakan program QCMP 116 yang dijalankan dengan IBM PC Compatible (Pentium III, 660 MHz) telah dilakukan. Permukaan ini terdiri dari 20 atom dengan tiga lapisan. Sebuah NH₃ (dengan bidang molekul planar dibuat sejajar atau tegak lurus bidang permukaan), pada berbagai posisi jatuh dioptimasi tiga dimensi dengan program tersebut. Hasil perhitungan binding energi NH₃ (BE(NH₃)) pada permukaan dan panjang ikatan antar atom pada kondisi optimal memperlihatkan: molekul NH₃ dengan bidang molekul sejajar bidang permukaan menuju atom permukaan lapisan satu dan tiga, teradsorpsi kimia lemah dengan rentang BE(NH₃) 0,9797 – 1,3421 eV/molekul dan yang menuju lapisan kedua diuraikan oleh permukaan. Molekul NH₃ yang mendatangi permukaan dengan bidang molekul tegak lurus permukaan teradsorpsi secara fisika (sangat lemah) mempunyai rentang BE(NH₃) 0,4903 – 0,5614 eV/molekul.

Kata Kunci : Adsorpsi, Energi ikatan

ABSTRACT

Interactions of an NH₃ molecule on chromium(111) surface has been studied by QCMP 116 program, runs on IBM PC compatible (Pentium III, 660 MHz). This surface consists of 20 atoms with three layers. 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 oriented to atoms of the first and third layer and one of its NH bond parallel to the Cr-Cr bond were chemisorbed molecularly with BE(NH₃) in range of 0.9797 – 1.3421 eV/molecule and to the second layer 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 Cr atom) was adsorbed physically with BE(NH₃) in range of 0.4903 – 0.5614 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 yield. Norskov and Stoltze¹ reported that N₂ was adsorbed atomically to iron surface, followed by reaction to 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 and 400 times more active than the Fe(100) and Fe(110) surface, at 200 atm and 525°C², respectively. Dowben et al³ found that N₂ was adsorbed molecularly and atomically on Cr(110) surface.

This is not surprising, since both Fe and Cr have the same crystal structure i.e body centered cube (bcc) with a₀ (lattice parameter) 2.78 and 2.88 Å, respectively. Kusuma⁴ also found that N₂ was adsorbed atomically on Fe(111), Fe/Cr(111) (alloy Fe-Cr), and Cr(111).

The aim of this investigation was to study the BE(NH₃) on the Cr(111) surface. It was defined that the binding energy of NH₃ on the surface was (BE(NH₃)). 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 (Figure 1). Then an NH₃ with molecular plane parallel (NH₃ parallel) and perpendicular (NH₃ 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, runs on IBM PC compatible (Pentium III), with accuracy 0.00001 eV. In this calculations, an NH_3 molecule was assumed to be planar with $d(\text{N-H}) = 0.992 \text{ \AA}$, and $\angle \text{HNH} = 120^\circ$ (D_{3h}).

METHODOLOGY

Formerly EMO method worked on mainframe. In order to get more applications, this program was modified as ASED program (work 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 propose, some of its atomic parameters were modified.

The inputs of this program were number of atoms, coordinate of each atoms and atomic parameters of those atoms. The atomic parameters were : the 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 were two types of orbital exponent (ξ_1 and ξ_2), and two types 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 were modified by Kusuma⁶. The coordinate to be used in these calculations was internal coordinate.

Outputs of this program were the total energy of system (E_T in eV), and distance matrices that give information about interatomic distance (d in \AA), overlap population matrices, that reflect the strength of interatomic bond, etc. Detail about the program is written in the manual of the program (Calzaferri and Brandle, 1992).

The surface to be studied was shown in Figure 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 $d(\text{Cr-N})$ initial = 1.5 \AA ; No 13, 16 (in second layer), No 11, 18 (in third layer) both with $d(\text{Cr-N})$ initial = 1.0 \AA . It also had been oriented to the middle point between two atoms with $d(\text{Cr-N})$ initial = 1.0 \AA . 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 $d(\text{Cr-N})$ initial = 1.0 \AA). During 3 D optimization (manual) surface was assumed to be rigid. Optimization begun with N atom followed by H atoms, simultaneously. At the beginning, for each set of optimization the increment / decrement of the vector length was assumed to be 0.1 \AA , while for bond angle and dihedral angle were 2° . When we got close to the optimized condition, those values were changed to 0.001 \AA and 0.05° , respectively. In some cases, to keep the NH_3 molecule not to leave the surface immediately, we defined that at the first step of optimization the length of vector N should not be greater than 2.200 \AA .

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. This was due to $\text{BE}(\text{NH}_3)$ reflected strength of surface to adsorb the NH_3 molecule, indirectly the possibility of a surface to desorb the adsorbed NH_3 . $\text{BE}(\text{NH}_3)$ was calculated by :

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

Table 1. The parameter used in the present calculations

Atom	ns	ξ_s	VSIE (eV)	np	ξ_p	VSIE (eV)	nd	ξ_1	VSIE (eV)	ξ_2	C1	C2
Cr	4	1.600	-8.77	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

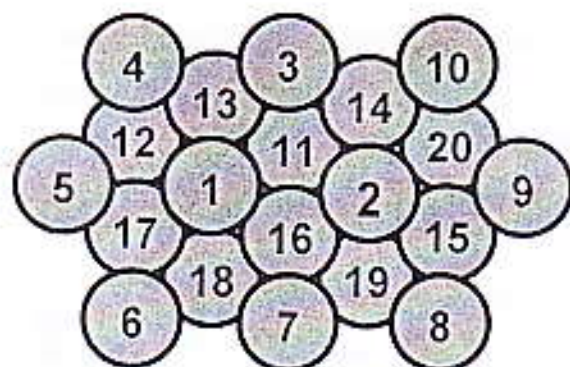


Figure 1. Cr(111) surface; 1-10 : first layer; 13-17 : second layer; 11, 12, 18-20 : third layer

RESULTS AND DISCUSSIONS

Table 2 showed the results of these calculations. An NH_3 parallel usually was chemisorbed molecularly with $\text{BE}(\text{NH}_3)$ and $d(\text{Cr-N})$ 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 Å⁷, respectively. It might be Cr(111) desorbed the adsorbed NH_3 better than Fe(111) surface.

Table 2. $\text{BE}(\text{NH}_3)$ and internuclear distances of An NH_3 oncoming with molecular plane parallel and perpendicular to the Cr(111) surface at many positions.

No	Posisi	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	// $\frac{1}{2}$ (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	// $\frac{1}{2}$ (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	// $\frac{1}{2}$ (1-7), 1-2	1,8920 (7)	-	1,0050	1,6134	1,0215
10	// $\frac{1}{2}$ (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	// $\frac{1}{2}$ (1-16), 1-16'	1,8930 (1)	-	1,0050	1,6134	1,0216
13	// $\frac{1}{2}$ (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	// $\frac{1}{2}$ (8-9), 1-2	1,9180 (8)	-	1,0042	1,6141	0,9797
16	⊥ $\frac{1}{2}$ (1-2), $\text{NH} \rightarrow 1$	2,2901 (1)	-	0,9850	1,7060	0,4903
17	⊥ 9, $\text{NH} \rightarrow 9$	2,2979 (10)	-	0,9860	1,7078	0,5614
18	⊥ 1, $\text{NH} \rightarrow 1$	2,3142 (2)	-	0,9860	1,7061	0,4668
19	⊥ 7, $\text{NH} \rightarrow 7$	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	// $\frac{1}{3}$ (16), 1-16'	N - H Bond was broken				
23	// $\frac{1}{2}$ (7-8), 1-2	N - H Bond was broken				
24	// $\frac{1}{2}$ (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

$\frac{1}{2}$ (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 internuclear distance of N atom to atom No 8 is 2,3202 Å

There were two types of bonding structure of NH_3 parallel on $\text{Cr}(111)$ surface, **a** and **b** (Figure 2). Structure **b** had $\text{BE}(\text{NH}_3)$ 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 were reactive. Some of edge positions also adsorbed NH_3 with structure **a** with $\text{BE}(\text{NH}_3)$ less than of and $d(\text{Cr-N})$ 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 $d(\text{N-H})$ was greater than

2.3 Å. As a result the calculated binding energy was not the $\text{BE}(\text{NH}_3)$ (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 molecularly (No 3, with structure **b**. No 8 with structure **a**)

Sometimes (not often) structure **b** was also observed on $\text{Fe}(111)$, when an NH_3 parallel came to the edge site. Usually the probability to get structure **a** \gg **b** for $\text{Fe}(111)$. Generally, the NH_3 perpendicular was adsorbed physically (Table 2, No 16 - 19) with $\text{BE}(\text{NH}_3)$ an $d(\text{Cr-N})$ in the ranges of 0.4903 – 0.5614 eV/molecule and 2.2901– 2.3202 Å, respectively. Their $\text{BE}(\text{NH}_3)$ was less than $\text{BE}(\text{NH}_3)$ that chemisorbed molecularly and $d(\text{N-H})$ around 2.3 Å. The same results were observed for $\text{Fe}(111)$ surface⁷.

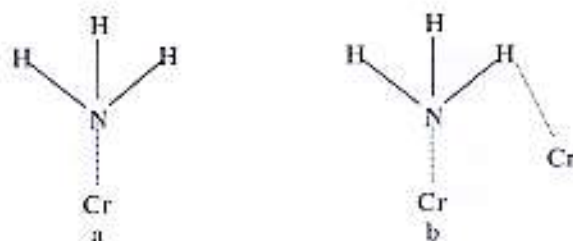


Figure 2. Suppose structures for the adsorption of ammonia to the Chromium metal

CONCLUSIONS

Structure **b** had $\text{BE}(\text{NH}_3)$ greater than **a**, since two atoms of the NH_3 molecule were bonded to the different Cr atom of the surface. More structure **b** were observed on edge site than edge position. It was assumed that $\text{Cr}(111)$ surface might desorb ammonia molecule better than $\text{Fe}(111)$, since $\text{BE}(\text{NH}_3)$ for $\text{Cr}(111)$ was less than $\text{Fe}(111)$.

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