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Adsorption and decomposition of FCN on Si (100)-(2×1) surface: A density functional theory study

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Abstract

The adsorption and decomposition of FCN on Si (100)-(2×1) surface have been studied by using density functional theory with the cluster model. Si_9H_{12} dimer cluster is used to simulate the Si (100) surface. The present calculations show that FCN can be adsorbed without a barrier on the surface with linear (L1) or parallel (S1) model. L1 can further isomerize to S1 with a barrier of 13.2 kcal mol^{-1}. Unlike HNC, ClNC, INC and FCN absorbed on Si (100) with a linear structure, FNC is absorbed on the Si (100) surface with a bend structure. Both FCN and FNC end-on adsorbates are dissociated readily to F and CN species.

Keywords: Density functional theory; Adsorption; Decomposition; FCN; FNC; Si (100) surface

1. Introduction

The studies of the reactions of CN-containing on solid surfaces are an important topic in many fields. Important industrial processes, such as the Andrussov reaction, depend on the reactivity of the CN bond [1]. The chemistry of cyanide is also important to understand the surface chemistry of C and N containing systems [2]. In the past decade, most of experimental and theoretical studies are about the adsorption of CN-containing molecules on the transition metal surfaces [2,3]. There are also some experimental and theoretical reports about CN-containing molecules adsorption on semiconductor Si surface [4–15]. Understanding the mechanism of the reactions of small molecules containing C, N with Si surfaces is not only fundamentally interesting but also practically important to the chemistry of SiX (X=C, N, or CN) and diamond thin-film deposition [4].

Based on the experimental report [5], Lin's group [4,9] has studied the adsorption and decomposition of HCN on Si (100)-(2×1) by using density functional theory (DFT) calculations with the Si_9H_{12} dimer cluster model. Their results showed that the HCN could be adsorbed molecularly without a barrier onto the surface with both end-on and side-on positions. Both HCN and HNC end-on adsorbates were dissociate readily to H and CN adspecies [4,9], and in good agreement with the experiment [5]. Similar results were obtained for ClCN and ClNC on the Si (100) surface [10].

Recently, Materer and co-workers have studied the adsorption and decomposition of cyanogen halides (XCN, X=Cl, Br, I) on Si (100) surface by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and temperature programmed desorption (TPD) spectroscopy [11,12]. For submonolayer exposure, XPS indicates that the CN triple bond of XCN remains intact upon adsorption at 100 K. The UPS spectrum contains two peaks assigned to the π-electrons in the CN triple bond [11,12]. Materer and co-workers [13,14] also studied the adsorption and surface reactions of XCN (X=Cl, Br, I) on Si (100)-(2×1) by ab initio quantum calculation on single- and triple-dimer silicon clusters. The calculated results showed that cyanogen halides can physisorb via a dative bond through the N atom. And this species can further react to form either a dissociated state through X–CN bond cleavage or a stable side-on intermediate by reacting across

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the dimer bond [13,14]. Materer et al. [14] also suggested that the adsorption energy decreases with increasing halide electronegativity. It is well known that fluorin atom has the strongest electronegativity at halogen atoms. In XCN (X=F, Cl, Br, I) molecules, F atom has some negative charges, on the contrary, other halogen atoms have some positive charges [10]. Therefore, it would be interesting to know, with increasing halide electronegativity, whether the adsorption energy of FCN on Si (100) surface is the lowest for XCN (X=F, Cl, Br, I) on Si (100) surface.

However, to our knowledge, the adsorption and decomposition of FCN on Si (100)-(2×1) surface have not been studied in the experimental and theoretical works. It is important that, the theoretical investigations for the adsorption and decomposition of FCN on Si (100) surface can provide a wealth of information about the properties of surfaces, such as the configurations, bonding mechanisms and vibrational frequencies etc., and these information can further help us understand the difference of halogenocyanogen (XCN, X=F, Cl, Br and I) and HCN on the Si (100) surface.

In present work, we study that the adsorption of FCN and FNC on Si (100)-(2×1) by using DFT method with the cluster model. Our theoretical approach allows us to optimize the geometry of adsorbed FCN and FNC and to calculate accurately the adsorption energies and reactive paths of FCN and FNC on the Si (100) surface.

2. Theoretical model and calculational approach

We have used a Si_9H_{12} model to represent the reconstructed Si (100)-(2×1) surface. The Si_9H_{12} model is a single-dimer cluster, where the top layer is a dimer consisting of two Si atoms, each with one dangling bond. The equilibrium geometries of the FCN and FNC molecules and the corresponding stretching frequencies were obtained from the density functional calculations. The calculations were performed by using the hybrid density functional method including Becke's 3-parameter nonlocal-exchange functional [16] with the correlation functional of Lee–Yang–Parr [17] (B3LYP) as in the GAUSSIAN 03 suite of programs [18]. The Si and H were described using a 6-31G* basis set. For FCN and FNC, all electrons were explicitly considered within the 6-31G(2df) including the polarization d-function and f-function, which was previously found to provide acceptable results at a reasonable computational cost [10]. Adsorption energies were calculated as the difference between the total energy for supersystem, cluster-FCN, and total energies of the cluster model and the isolated FCN molecule obtained by using the same basis set.

In this paper, all atomic positions are full optimized without geometry constraints. Frequency calculations confirm that the stable geometries have real vibrational frequencies. The transition states contain only one imaginary normal mode.

3. Results and discussion

3.1. The molecular properties of gas-phase FCN and FNC

Table 1 lists the present calculated molecular properties for gas-phase FCN and FNC, and relative total energies (ΔE) between FCN and FNC. All energies are relative to FCN. Table 1 also includes optimized gas-phase FCN and FNC geometries and energies performed by Lee and coworkers [19] using a coupled cluster method CCSD(T) (including both single and double substitutions, and triple

Table 1
Molecular properties for gas-phase FCN and FNC

	Ground state FCN, $^1\Sigma^+$			Ground state FNC, $^1\Sigma^+$		
	This work	CCSD(T)[a]	Exp.	This work	CCSD(T)[a]	Exp.
ΔE (kcal mol^{-1})[b]	0.0	0.0		68.1	70.2	
$R_{C\text{–}N}$ (Å)	1.1552	1.1632	1.157[c]	1.1770	1.1842	
$R_{F\text{–}C}$ (Å)	1.2619	1.2701	1.264[c]			
$R_{F\text{–}N}$ (Å)				1.3002	1.3097	
∠FCN (°)	180.0		180.0			
∠FNC (°)				180.0		180.0
$\nu_{C\text{–}N}$ (cm^{-1})	2343[d]	2350	2319[e]	2155[d]	2158	2123[f]
$\nu_{C\text{–}F}$ (cm^{-1})	1074[d]	1079	1076[e]			
$\nu_{N\text{–}F}$ (cm^{-1})				961[d]	948	928[f]
ν_{FCN} (cm^{-1})	496[d]	451	451[e]			
ν_{FNC} (cm^{-1})				267[d]	200	

[a] Ref. [19].
[b] Energy with zero-point energy corrections.
[c] Ref. [20].
[d] Frequency scale factor is 0.96.
[e] Ref. [21].
[f] Ref. [22].