C1s CEBEs of Hydrocarbons on Elemental Oxides. I. MO Calculations using CH_4 Model Molecules

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(Received April 13 1999; accepted May 12 1999)

Practical C1s core-electron binding energies(CEBEs) of hydrocarbons, alcohols or organic acids(which contain $C_nH_{2n+1(n=5\text{-}16)}$ – group) on elemental oxides are determined as 284.7, 286.3 and 285.2 eV on B_2O_3, Al_2O_3 and SiO_2, respectively. The results indicate that the CEBEs are more or less larger than 285.0 eV as the value relative to the C1s of polyethylene, when the organic molecules adsorb on the oxygen atom of the elemental oxide. We will, thus, perform deMon density-functional calculations for C_2H_5/(BH_2O, AlH_2O, SiH_3O) chemical bonding molecules and CH_4/($B_2H_4O_3$, $Al_2H_4O_3$,$Si_2H_6O_3$) bimolecular interaction types, in order to examine above which atom in elemental oxide the carbon is located. For the geometry of the molecules and the bimolecular interaction system, we used the optimized cartesian coordinates from semiempirical AM1 (version 6.0) method. Furthermore, the basis sets, 4-31G and 6-31G, were used for optimization of the interaction system involving second-and third-period atoms, respectively, again by HONDO program (version 7.0), based on the semiempirical MO data.

Introduction

For adsorbed hydrocarbon, alcohol, or organic acid molecules, two types of interactions are usually considered as chemical bonds (mainly with the surface oxygen atoms of the elemental oxide), or van der Waals interactions and/or weak polarization bonds with surface atoms. We will investigate the interaction of adsorbed hydrocarbon, alcohol or organic acid molecules on the elemental oxides(B_2O_3, Al_2O_3 and SiO_2) in comparison of the theoretical core-electron binding energies (CEBEs) by deMon density-functional calculations [1] with experimental values.

Experimentally, practical C1s CEBEs of hydrocarbons, alcohols, or organic acids (which contain $C_nH_{2n+1(n=5\text{-}16)}$–group) as contaminants on elemental oxides were determined as 284.7, 286.3 and 285.2 eV on B_2O_3, Al_2O_3 and SiO_2, respectively, within a resolution of 0.1 eV. The CEBEs were obtained from naturally formed native oxides by charge referencing to the true CEBEs of the pure elements in the native oxide. On the other hand, accurate computations of the CEBEs of simple molecules were performed with an average absolute deviation for C1s, N1s and O1s levels of only 0.2 eV by Chong [2-4], as based upon the unrestricted generalized transi-tion state model (uGTS). This procedure has been tested on about CEBEs of a hundred of molecular systems ranging from small molecules to larger models (n-unit models of polymers, n=1-3) [5-10].

In order to account for solid-state effects, a quantity WD is subtracted from computed CEBEs. This quantity WD denotes the sum of the work function of the sample and other energy effects, as indicated in previous works [7-9]. In the case of polymers, the experimental WDs can be estimated from differences between C1s CEBEs of monomers or oligomers(and corresponding to "gas-phase" situations), and experimental binding energies of actual polymer. For polyethylene (PE), the value was given as 5.3 eV between 290.3 eV of $C_{13}H_{28}$ in gas [11] and 285.0 eV of polyethylene [12], and in the case of poly(methyl methacrylate) (PMMA), the WD was calculated as 5.8 eV of the difference between the CEBEs of methyl isobutyrate[13] and of PMMA[12].

In the present study, small cluster model are

first considered to mimick the bare elemental oxide surfaces (BH_2O, AlH_2O, SiH_3O). In the model molecules, the dangling bonds are terminated by hydrogens. For each system, the theoretical CEBEs of the various available core levels (O1s, B1s, Al2p and Si2p) are compared to the experimental findings, and a series of WD values is obtained (Table 1). The mean WD value for each system is then used straightforwardly in the systems describing the interaction of alkane with the oxide surface: either in a chemisorption (C_2H_5/ BH_2O, AlH_2O, SiH_3O) or within physisorption conditions(CH_4/ $B_2H_4O_3$, $Al_2H_4O_3$, $Si_2H_6O_3$).

Theoretical Details

In the generalized transition-states(GTS) method, Williams et al.[14] proposed the extension of Slater's transition-state idea[15] and approximated the endothermicity $\Delta E = E(1) - E(0)$ by

$$\Delta E = [F(0) + 3F(2/3)]/4 \quad , \qquad (1)$$

where $F(x)=\delta E(x)/\delta x$, and $x(0<x\leq 1)$ is assumed to be a continuous variable, with E(0) and E(1) denoting the energies of the initial and final states, respectively. For example, for the ionization of an electron from molecular orbital (MO) ϕ_k of interest, x represents the fraction of electron removed, and, according to the Janak theorem [16], F(x) is the negative orbital energy $\varepsilon_k(x)$. This procedure is applied in the following way. In the unrestricted generalized transition-state(uGTS) method, we removed 2/3 α electron from MO ϕ_k of interest.

For the geometry of the molecules and the bimolecular interaction system, we used the optimized cartesian coordinates from semiempirical AM1 (Version 6.0) method [17] using experimental parameters at 25 °C for two-center integrals in Hartree-Fock SCF equation. The AM1 geometries have then been used as starting points for further RHF optimization using HONDO (Version 7.0) [18], using the 4-31G and 6-31G split-valence basis sets, one after the other. We computed the CEBEs on these optimized geometries, by the deMon density functional theory (DFT) calculations[1].

The deMon calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Becke's 1988 exchange functional[19] and Perdew's 1986 correlation functional[20]. In the program, we used a non-random grid and a scaled polarized valence triple-zeta (scaled-pVTZ) basis set [4,7]for B, C, O, Al, Si, and H with auxiliary fitting functions labeled (4,4;4,4) for B, C and O, (5,4;5,4) for Al and Si, (3,1;3,1) for H. In the case of van der Waals interaction, we used aug-cc-pVTZ basis set for C and each atom of EOs in the intermolecular distance range of more than 2.5 A, although we may neglect the effect of temperature.

Experimental

The measurements were performed on the SSI XPS system with a cryopump. The cryopump was regenerated every 3-5months to remove unwanted gases. The ultimate pressure was 5×10^{-10} torr when the electron guns were off. The X-ray source was monochromated Al Kα radiation (1486.6 eV). The energy scale was calibrated every 2-4 weeks by using Ag 4f7 83.98(±0.08) eV, Cu2p3 932.67(±0.08) eV and Ag3d5 932.28 (± 0.08) eV lines.

Practical C1s CEBEs of hydrocarbon, alcohol, or organic acid (which contains $C_nH_{2n+1(n=5\text{-}16)}$ – group) as contaminants on elemental oxides were determined as 284.7, 286.3 and 285.2 eV on B_2O_3, Al_2O_3 and SiO_2, respectively, within a resolution of 0.1 eV. The C1s CEBEs were obtained from naturally formed native oxides by charge referencing to the true CEBEs of the pure elements in the native oxide. Three different experiments were performed on the same sample, to obtain the practical CEBEs in the following way:

1) The sample was grounded and analyzed with the charge neutralizer turned off.
2) The sample was floated on glass and irradiated with the charge neutralizer set to minimum voltage (ca. 2eV) and minimum current.
3) The sample was floated on glass and irradiated with the charge neutralizer set to near maximum voltage(ca 16 eV) and near maximum current.

The CEBEs from floated sample were collected by using the energy difference between the experimentally measured CEBEs of pure elements in the native oxide when the floated

native oxide sample grounded and floated on glass. The practical C1s CEBEs were averaged out from the values obtained under the three different experimental conditions.

Results and Discussion

a) *CEBEs and WDs of elemental oxides*

We considered model molecules, $B_2H_4O_3$, $Al_2H_4O_3$, $Si_2H_6O_3$ for elemental oxides, to obtain the WDs due to the solid-state effect. Table 1 shows the experimental CEBEs of elemental oxides and calculated CEBEs of the model molecules. We will thus adopt the assumed WD of each atom in the elemental oxide from the differences between CEBEs of model molecules in gas and of the elemental oxide in Table 1.

Table 1. CEBEs of elemental oxides and the model molecules, and the assumed WDs

elemental oxides	CEBEs obsd. (eV)	model molecules	CEBEs calc. (eV)	WD (eV)
B_2O_3		$B_2H_4O_3$		
O1s	532.5	O1s [-O-]	538.85	6.4
		O1s [-OH]	539.37	6.9
B1s	193.9	B1s	—	—
Al_2O_3		$Al_2H_4O_3$		
O1s	531.1	O1s [-O-]	537.07	6.0
		O1s [-OH]	537.98	6.9
Al2p	74.4	Al2p	81.59	7.2
SiO_2		$Si_2H_4O_3$		
O1s	532.5	O1s [-O-]	538.27	5.8
		O1s [-OH]	538.75	6.3
Si2p	103.0	Si2p	108.91	5.9

b) *Van der Waals interaction types*

One of the structures of bimolecular interaction systems between CH_4 and the model molecules of the elemental oxide(EO)s ($B_2H_4O_3$, $Al_2H_4O_3$, $Si_2H_6O_3$) was shown in Fig. 1. We systematically varied the H-CH_3 –O(or X(= B, Al, Si)) (of EOs) length to obtain the optimization energy of the interaction systems. The intermolecular distances between methane carbon and each atom of EO model molecules(The carbon approaches each atom of EO chains perpendicularly in the plane of Fig. 1.) for energy optimization were also obtained in Table 2 for CH_4/($B_2H_4O_3$, $Al_2H_4O_3$, $Si_2H_6O_3$) bimolecular interaction types, respectively from ab initio MO calculations using HONDO program.

In Table 2, we showed the calculated C1s CEBEs using uGTS method for the bimolecular interaction types with the experimental values of the organic molecules on the elemental oxides. Although we used simple model molecules for the interaction systems, calculated C1s CEBEs of CH_4/($B_2H_4O_3$, $Si_2H_6O_3$) types seem to correspond to the experimental CEBEs within 0.9 eV. On the other hand, the calculated CEBEs of $CH_4/Al_2H_4O_3$ were underestimated as 283.3 to 284.2 eV less than the observed values, 286.3 eV. We can, thus, assume that the latter case does not belong to the physisorption geometry. These interaction systems will be clarified using the cluster model of the elemental oxides in a forthcoming paper.

Fig.1 One of the geometrical structures for bimolecular interaction systems between methane and the model molecules of elemental oxides.

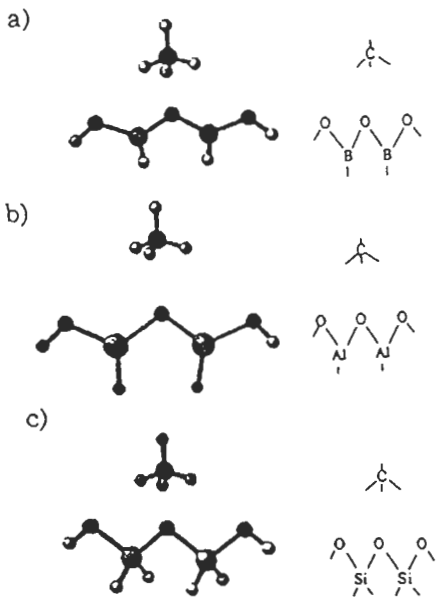

Table 2. C1s CEBEs of hydrocarbons on elemental oxides and of the model molecules

hydrocarbons(HC) on elemental oxide	C1s CEBEs obsd. (eV)	CH_4 on the oxygen of model molecules		C1s CEBEs calc. (eV)	(CEBE)-WD (eV)
HC/B_2O_3	284.68	$CH_4/B_2H_4O_3$			
		on [-O-]	(R=3.66 Å)	290.27	283.9
		on [-OH]	(R=3.73 Å)	290.43	283.5
HC/Al_2O_3	286.33	$CH_4/Al_2H_4O_3$			
		on [-O-]	(R=4.45 Å)	290.24	284.2
		on [-OH]	(R=3.83 Å)	290.53	283.6
		on [-Al-]	(R=5.32 Å)	290.49	283.3
HC/SiO_2	285.19	$CH_4/Si_2H_4O_3$			
		on [-O-]	(R=4.52 Å)	290.37	284.6
		on [-OH]	(R=3.75 Å)	290.66	284.4
		on [-Si-]	(R=5.32 Å)	290.61	284.7

c) *Chemical bonding types*

For polymers of the carbon single-bonded to a oxygen, the C1s CEBE is observed as 285.8 to 287.0 eV[12]. We, then, considered these chemical bonding types as the elemental oxide, $(XH_{(2\ or\ 3)}O)$-C_2H_5 molecules. Table 3 shows the theoretical CEBE due to solid-state effect as (CEBE) - WD using the differences between CEBEs of O1s of the bonding molecules and the observed ones of pure elemental oxides. For the AlH_2O-C_2H_5, the calculated C1s CEBE is in good accordance with the value of organic molecules on Al_2O_3. This indicates that organic molecules undergo dissociative chemisorption on Al_2O_3, while it may be merely physisorbed on SiO_2 and B_2O_3.

Table 3. C1s CEBEs of hydrocarbons on elemental oxides and of $(XH_{(2\ or\ 3)}O)$-C_2H_5 chemical bonding molecules

hydrocarbon(HC) on elemental oxide		CEBEs obsd. (eV)	$XH_{(2\ or\ 3)}O$-C_2H_5 molecule	CEBEs calc. (eV)	(CEBE)-WD (eV)
HC/B_2O_3			BH_2O-C_2H_5		
	C1s	284.68	C1s [-CH_2-]	292.64	286.2
			C1s [-CH_3]	291.19	284.7
	O1s	(532.5)	O1s	(538.99)	
HC/Al_2O_3			AlH_2O-C_2H_5		
	C1s	286.33	C1s [-CH_2-]	292.17	286.0
			C1s [-CH_3]	290.69	284.5
	O1s	(531.1)	O1s	(537.27)	
HC/SiO_2			SiH_2O-C_2H_5		
	C1s	285.19	C1s [-CH_2-]	292.17	287.4
			C1s [-CH_3]	290.91	286.1
	O1s	(532.5)	O1s	(537.27)	

In comparison of theoretical C1s CEBEs for the two types of the interactions using model molecules with the experimental values, the types for organic molecules on elemental oxides can be classified as;

a) organic molecules on B_2O_3 and SiO_2 may be a van der Waals interaction or weak polarization bond type(physisorption geometry),

Table 4. C1s CEBEs and the absolute errors of hydrocarbons on elemental oxides and of $(XH_{(2\ or\ 3)}O)$-C_2H_5 chemical bonding molecules

	obsd.	physisorbed (a) calc.	dev.	chemisorbed (b) calc.	dev.
HC on B_2O_3	284.68	283.9	-0.8	286.2	+1.5
HC on Al_2O_3	286.33	284.2	-2.1	286.0	-0.3
HC on SiO_2	285.19	284.6	-0.6	287.4	+2.2

(a) from Table 2

(b) from Table 3

b) organic molecules adsorbed on Al_2O_3 are considered as a chemical bonding type.

Further theoretical studies on the interaction system using the cluster models are in progress.

Acknowledgement

We thank Dr. B. V. Crist of XPS International very much for his suggestions and provisions to us in all XPS experiments.

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Referee's comments
: Associate Professor K. Takahashi(Tokyo Institute of Technology)

This paper shows an interesting comparison of core-electron binding energies (CEBEs) and should be published in JSA. However, the authors should mention following 3 point.

(1). Authors use the model molecules $B_2H_4O_3$,$Al_2H_4O_3$, and $Si_2H_6O_3$. In these molecules, dangling bonds are terminated by hydrogens. This model would have made the calculations easy (in problem of degeneracy). However, the charge transfers are different between the bonds Al-O, Al-H, and Al-Al, for example. The electronic structure of the model is different from practical one. It may be fatal. (Of course, it may be negligible. Many similar works are expected.)

(2).In the subsection b) in the section of "Results and Discussion", author write procedure to find an optimum geometry between molecules. When CH_4 is approaching to Al(, B, or C), the results would be different from the case that CH_4 is approaching to the central Al of " $Al_3H_5O_4$". The calculation for $Al_2H_4O_3$ is affected by the charge transfer by OH at the side end of the molecule. Similar effect can be easily considered for also $B_2H_4O_3$, and $Si_2H_6O_3$. Taking account of these fact, this work has an importance, because this work shows a information for some cases. All optimum geometries in calculation have to be clearly expressed.

(3). The calculation is of zero temperature while the measurement is done at room temperature. In case of week bond such as Van der Waals interaction, the effect of temperature is larger than usual tight binding molecular, because the position of core atom (ion) is easy to move.

Author has estimated it negligible ? Author should mention this point at least.

Authors' answers

Thank you very much for referee's comments.

(1) We added a following sentence in Introduction: "*In the model molecules, the dangling bonds are terminated by hydrogens.*" It must be clear for our models, as commented by the referee.

In the case of effects of the charge transfers, we neglected the small contributions to the inter-actions, since the absolute error between the calculations of this model and experimental values is estimated as 0.5 eV.

(2) We rewritten the sentence for the geometry optimization **in b) of Results and Discussion** as follows:

"The intermolecular distances between methane carbon and each atom of EO model molecules (The carbon approaches each atom of EO chains perpendicularly in the plane of Fig. 1.) for energy optimization were also obtained in Table 2 for CH_4/($B_2H_4O_3$, $Al_2H_4O_3$, $Si_2H_6O_3$) bimolecular interaction types, respectively from ab initio MO calculations using HONDO program."

(3) We may neglect the temperature effect. However, the geometry optimization using AM1 program depends upon the results at 25 °C. For van der Waals interaction of these models, we used aug-cc-pVTZ basis set. For this description, the following sentences are rewritten in **Theoretical Details**:

"For the geometry of the molecules and the bimolecular interaction system, we used the optimized cartesian coordinates from semiempirical AM1 (Version 6.0) method [17] using experimental parameters at 25 °C for two-center integrals in Hartree-Fock SCF equation."

"In the case of van der Waals interaction, we used aug-cc-pVTZ basis set for C and each atom of EOs in the intermolecular distance of more than 2.5 A, although we may neglect the effect of temperature.."