*C1s CEBEs of Hydrocarbons on Elemental Oxides. II. The Adsorption Type of CH_4 on the MgO Cluster

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Experimental C1s core-electron binding energy (CEBE) of hydrocarbons, alcohols or organic acids, which contain C_nH_{2n+1}-functional group, on MgO is determined as 286.5 eV. The value is larger than 285.0 eV as the standard value relative to the C1s CEBE of polyethylene. We discuss the physisorption type of CH_4 on the MgO clusters from theoretical viewpoints of both ab initio molecular orbital (MO) and density-functional theory (DFT) calculations. We try to indicate whether the organic molecules physisorb on MgO, or not, using accurate computational results of CEBE by the DFT calculation.

1. Introduction

It is well known that metal oxide surfaces play a very important role on surface reaction and/or catalytic reaction. One has been interested in the characterization of adsorbates on such metal oxides and has tried to control the chemical reaction. Although there are many experimental researches on the adsorption and interaction with such metal oxide surfaces using IR, EELS, UPS, XPS, and so on, it is still difficult to understand the fundamental process of the adsorption and the chemical dissociation between adsorbates and surfaces.

A lot of studies on the adsorption on MgO surface have been done widely, because it shows the complex behavior during the reaction in spite of the quite simple crystallographic structure. For example, the adsorption of water on MgO (001) surface has been intensively studied experimentally [1-3] and theoretically [4-8], in order to determine the conditions that favor physisorption vs chemisorption of molecular water or chemical dissociation.

In our previous work [9], we have reported the prediction of interaction types by analyzing the accurate computational and experimental results. We have indicated the two types of interaction systems between elemental oxides (B_2O_3, Al_2O_3, SiO_2) and organic molecules in comparison of the theoretical C1s core-electron binding energies (CEBEs) by density functional theory (DFT) calculations with the experimental values. In the previous study, the elemental oxides, B_2O_3, Al_2O_3, and SiO_2 were modeled by very small and crude clusters, with the dangling bonds terminated by hydrogens. The models for physisorption systems were CH_4 on $B_2O_3H_4$, $Al_2O_3H_4$, and $Si_2O_3H_6$, respectively, while the chemisorption is modeled by H_2BO-C_2H_5, H_2AlO-C_2H_5, and H_3SiO-C_2H_5. By comparing the predicted CEBEs of adsorbed hydrocarbons with experiment, we were able to suggest that hydrocarbons are physisorbed on B_2O_3 and SiO_2 surfaces but are chemisorbed on Al_2O_3.

In the present study, we perform further theoretical investigation about the CH_4-MgO (001) interaction system. As was done in previous works, we examine the interaction types by accurate DFT calculation using cluster models. We use the MgO cluster model with the cubic structure, Mg_4O_4, as the minimal unit cell shown in Fig. 1(a). In this study, we report the results of the physisorption type between CH_4 and MgO(001) by using two model

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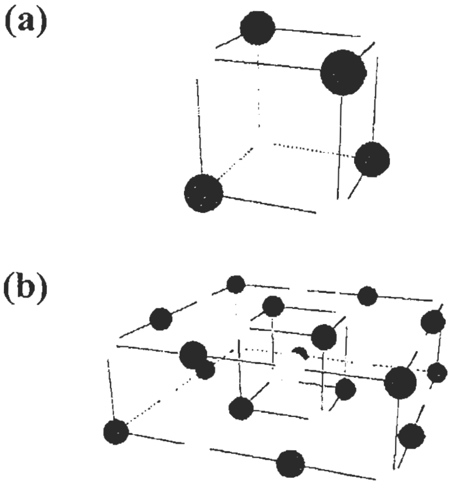

Fig. 1. Cluster models of (a) Mg_4O_4 and (b) $Mg_{16}O_{16}$.

structures, Mg_4O_4 and $Mg_{16}O_{16}$ in Fig. 1(a) and (b). The $Mg_{16}O_{16}$ cluster is just corresponding to the four-unit cells of the Mg_4O_4 cluster, of which the structure is reduced to the model-size dependency. From the accurate computation, the theoretical CEBEs of the available core levels (Mg2p, and O1s) are compared with the experimental ones, and the assumed shift values for each system are then used straightforwardly in the physisorption systems describing the interaction between alkane and the MgO surface. By comparing the predicted CEBEs with experimental ones of adsorbed hydrocarbons, we discuss whether the adsorbed hydrocarbons are physisorbed or chemisorbed on MgO surface.

2. Theoretical Background

As stated in the previous works [9], the theoretical CEBE calculation is computed by DFT calculation combined with the generalized transition state (GTS) method proposed by Williams and co-workers [10], which is the extension of Slater's transition state concept [11]. Within one-electron removal process, the vertical ionization energy was approximated by

$$E_{\lambda=1} - E_{\lambda=0} = \frac{1}{4}\left(\frac{\partial E}{\partial \lambda}\right)_{\lambda=0} + \frac{3}{4}\left(\frac{\partial E}{\partial \lambda}\right)_{\lambda=2/3},$$

where λ ($0 \leq \lambda \leq 1$) is assumed to be a continuous variable, with $E_{\lambda=0}$ and $E_{\lambda=1}$ denoting the total energies of the neutral molecule and cation, respectively. For the ionization of an electron from molecular orbital (MO) ϕ_k of interest, λ represents the fraction number of electron removed from the Kohn-Sham (KS) MO. According to Janak theorem [12], $\partial E(\lambda)/\partial \lambda$ becomes the negative KS orbital energy, $\varepsilon_k(\lambda)$. In the 'unrestricted' fashion of GTS (uGTS) method, the 2/3 electron was removed from the only α (or β) KS MO ϕ_k.

For the geometry optimization, we used the optimized cartesian coordinates from semiempirical AM1 (version 6) [13] for CH_4 molecule, and the interatomic distance between Mg and O, 2.105 Å for MgO cluster. In the CH_4-MgO(001) interaction system, the optimized structure was determined by considering two geometrical arrangements for CH_4 direction and three geometrical configurations between CH_4 and MgO cluster, using ab initio Gaussian 94 [14] program with 6-31G** basis set.

For the accurate computation of CEBEs, the best procedure as indicated in previous works [9] was used for DFT calculations, that is, the uGTS method combined with Becke's 1988 exchange functional and Perdew's 1986 correlation functional. The DFT calculation was performed by deMon-KS program (version 3.5) [15] with extrafine and nonrandom grid, and Dunning's correlation consistent polarized valence triple-zeta (cc-pVTZ) basis set for the neutral parent molecule and the same basis scaled for the atom with the partial core-hole (scaled-pVTZ) with auxiliary fitting functions labeled (5,4;5,4) for Mg, (4,4;4,4) for C and O, and (3,1;3,1) for H.

3. Results and Discussion

3.1. The computed CEBEs and the assumed WD of MgO

First, we discuss about the computed CEBEs and the assumed shift value, *WD* obtained by two cluster models. The energy value *WD* denotes the sum of the work function of the sample (*W*) and other energy effects (*Delta*), such as the polarization energy, the width of the intermolecular band formation, and the peak broadening in the solid state, and so on. In order to account for such solid-state

Table 1. CEBEs of MgO and the cluster model, Mg_4O_4 and $Mg_{16}O_{16}$, and assumed WDs.

	CEBE Observed (eV)		Cluster Model	CEBE Calculated (eV)		Assumed WD
MgO			Mg_4O_4			
	Mg2p	49.5		Mg2p	51.16	1.7
	O1s	529.8		O1s	533.21	3.4
			$Mg_{16}O_{16}$			
				Mg2p	50.70	1.2
				O1s	533.64	3.8

effects, the computed CEBEs have to be shifted by a quantity *WD*. Therefore, the predicted CEBE of adsorbed molecule on surface is obtained by the difference between the computed CEBE and the assumed *WD* obtained by metal oxides.

Table 1 shows the experimental CEBEs of MgO and the calculated CEBEs of the cluster models, Mg_4O_4 and $Mg_{16}O_{16}$. From the table, the assumed *WD*s of O1s and Mg2p were estimated as 3.4 and 1.6 eV for Mg_4O_4, and 3.8 and 1.8 eV for $Mg_{16}O_{16}$, respectively, from the differences between the calculated CEBEs of the cluster models and the experimental ones.

3.2. Physisorption System of CH_4 on MgO

Before considering the theoretical CEBEs of CH_4 on MgO, we seek the optimized structure of CH_4-MgO interaction system, exploring the structures of physisorption system between CH_4 and MgO cluster. In Fig. 2, we showed the two arrangements of CH_4 and MgO cluster models interaction type, (A) van der Waals type, and (B) hydrogen bond type. We systematically varied the distance between CH_4 and sites of the cluster model ((a) Mg-O, (b) Mg-Mg, and (c) O-O), in order to obtain the optimization energy of the interaction systems. The carbon of CH_4 approaches each atom (Mg or O) of cluster model perpendicularly.

Table 2 shows the intermolecular distances (Å) and the stabilization energies (kJ/mol). The stabilization energies are corrected with the basis set superposition error (BSSE). For the interaction types between CH_4 and MgO cluster models, the optimized structures were classified into (A) on the Mg atom in the van der Waals type, and (B) on the O atom in the hydrogen bond type. From table 2, we can also see that the van der Waals type is a favorable structure in the comparison with hydrogen bond type, because it has the positive stabilization energy (0.315 kJ/mol) in $Mg_{16}O_{16}$ cluster (B type). Thus we can consider the van der Waals type in the case of physisorption of CH_4 on MgO surface.

Table 2. Optimized intermolecular distances (Å), and stabilization energies for physisorption type.

Interaction Type		Intermolecuar Distance (Å)	Stabilization Energy	
			E (a. u.)	E (kJ/mol)
Mg_4O_4				
	A (on Mg)	3.1	-0.00048	-1.260
	B (on O)	3.8	-0.00034	-0.893
$Mg_{16}O_{16}$				
	A (on Mg)	4.1	-0.00061	-1.602
	B (on O)	4.1	0.00012	0.315

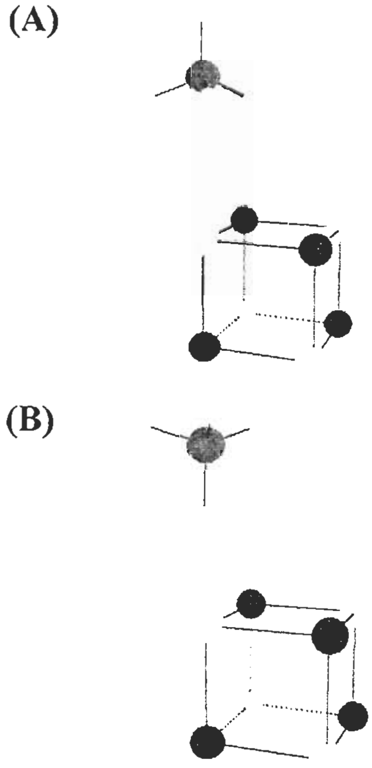

Fig. 2. One of the geometrical structures for the physisorption type, (A) van der Waals type, (B) hydrogen bond type.

3.3. C1s CEBE of CH_4 on MgO

Table 3. C1s CEBEs of hydrocarbons on MgO and of CH_4 on the cluster model, Mg_4O_4 and $Mg_{16}O_{16}$

CEBE Observed (eV)	Cluster Model	CEBE Calculated (eV)	CEBE – WD
Hydrocarbon-MgO	CH_4-Mg_4O_4		
C1s 286.46	A (on Mg)	C1s 290.82	289.2
	B (on O)	C1s 290.70	287.3
	CH_4-$Mg_{16}O_{16}$		
	A (on Mg)	C1s 290.67	289.5
	B (on O)	C1s 290.54	286.7

Table 3 shows the calculated C1s CEBEs using uGTS method for each interaction type with the experimental values of the organic molecules on the MgO surface. Table 3 also shows the theoretically predicted CEBEs due to solid-state effect as (CEBE – *WD*) using the differences between C1s CEBE of CH_4 and the assumed *WD*. We compared the predicted C1s CEBEs for the two types of the interactions using CH_4 and MgO cluster models with the experimental values in Table 3. Therefore, it could not be shown whether the organic molecules physisorb on MgO, or not, because the predicted C1s CEBEs in this study were fairly overestimated in Table 3.

4. Conclusion

We discussed the physisorption type of CH_4 on the MgO clusters from theoretical viewpoints of both ab initio MO and DFT calculations. The former MO results show that the physisorption of CH_4 on MgO is the van der Waals type, if the physisorption exists. However, we could not indicate whether the organic molecules physisorb on MgO, or not, from the latter DFT calculations. As the next step, we will consider the chemisorption type for the organic molecules on MgO (100) surface using DFT calculations.

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