Chemical Modification of MgO(001) Surface by Utilizing Energy Decomposition Analyses for the Purpose of CO_2 Adsorption

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The intermolecular interaction between a CO_2 molecule and an MgO cluster has been investigated by ab initio molecular orbital method in order to test a selection rule for chemical modifications of surfaces. Favorable adsorption geometry has been determined by partial geometry optimizations initiated from three possible formations of the molecular complex. A CO_3-form where the carbon atom is coordinated to an O atom of the MgO cluster is found to be most stable. The Kitaura–Morokuma energy decomposition analysis has been carried out to investigate the nature of the intermolecular interaction between a CO_2 molecule and an MgO cluster. It is found that charge transfer energy from the MgO cluster to CO_2 is the dominant component in the total stabilization energy. Two Mg atoms are replaced by two Ca atoms to enhance the electron flow from an MgO cluster to a CO_2 molecule, which resulted in the increase in the adsorption energy. The effect of the chemical modification is examined by the energy decomposition analysis. We confirm that the increase of the cohesive energy is a consequence of the increase in charge transfer interaction from the cluster to the CO_2 molecule. The mechanism of the charge transfer is also studied by the molecular orbital analysis.

Chemical modifications of solid surfaces have great technological relevance to separation processes in modern industry. Recent research has revealed that interactions between a surface and molecules play an important role in membrane separations.[1—3] In Ref. 1, Rao and Sircar suggested a permeation mechanism that can dominate for membrane separation i.e. the selective adsorption followed by surface diffusion. In order to improve the selectivity of a membrane, one should try to control or design the intermolecular interactions between adsorbates and surfaces by chemical modifications of the surfaces. It is also one of the most challenging problems in chemistry to control the molecular interactions by chemical modifications or molecular modelings for specific technological purposes. The approach of a molecule to a surface will cause electron redistributions in the molecule or the surface and this is the origin of the intermolecular interactions. We therefore have to solve the time-independent Schrödinger equation for electrons at a given nuclear geometry to get insight into the molecular interactions. In this work, ab initio molecular orbital calculations are employed to investigate the origin or the nature of the interactions between a molecule and a surface. In 1976, Kitaura and Morokuma proposed a variational method in which the total intermolecular interaction can be decomposed into various conceptually understandable terms, such as electrostatic, exchange, polarization, and charge transfer.[4] The total interaction energy itself is not a guide adequate for chemical modifications. However, each component obtained by the decomposition analysis will give us physically meaningful information on the molecular interactions, from which we can predict what kind of atoms or molecules should be introduced to the surface in order to increase adsorption energy. For example, in a case when charge transfer interaction from monomer A to monomer B is the dominant component in the total interaction energy, it is probable that the introduction of atoms that have small electron negativities will give rise to a larger charge transfer interaction and consequently a larger adsorption energy.

The MgO(001) surface has been extensively studied and known to be a good catalyst or adsorbent.[5—13] In the present study, Morokuma's energy decomposition analysis is employed to understand the molecular interaction between the MgO(001) surface and a CO_2 molecule when they are placed at their stable geometry. The selection rule that we suggest for chemical modification of surfaces is very simple. One should choose atoms that promote the dominant component of interactions obtained from the energy decomposition analysis.

Methods and Calculational Details

The MgO(001) surface is approximated by an Mg_8O_8 cluster depicted schematically in Fig. 1. Considering the electrostatic interaction formed by the fractional charges on each atomic site (plus charges on Mg and C atoms and minus charges on O atoms), we consider three stable adsorption configurations of CO_2 and the MgO cluster, as shown in Figs. 2(a), 2(b), and 2(c). We refer to these three types of geometry in Figs. 2(a), 2(b), and 2(c) as *ontop*, *bridging*, and *CO_3-form*, respectively. We performed partial geometry optimizations for each configuration by the energy gradient method. Optimized parameters are given in each figure. The geometry of the cluster is fixed at the crystal lattice positon with the MgO distance of 2.105 Å.[14] Relaxation of the MgO surface caused by the approach of the CO_2 molecule might be important in the chemisorption processes; however, to reduce the computational cost in the present study we did not consider the relaxation effect of the MgO sur-

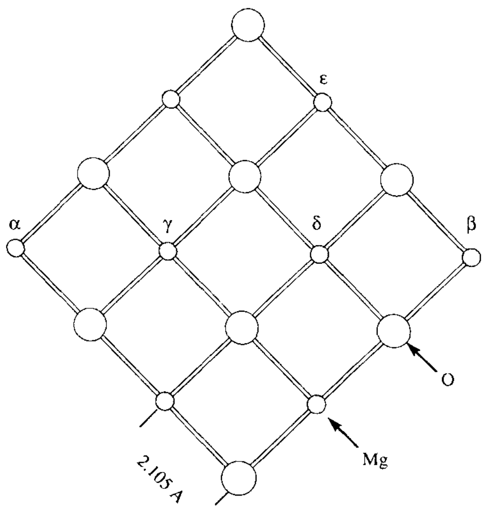
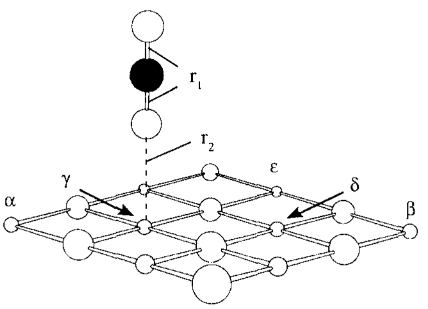
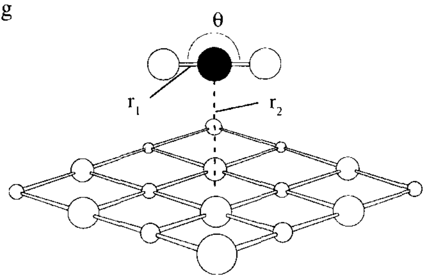


Fig. 1. Schematic representation of a Mg_8O_8 cluster model for MgO(001) surface. Mg–O bond length is 2.105 Å. The notations $\alpha, \beta, \gamma, \delta$, and ε are shown for the later references to specify the sites where the replacements are done.

(a) ontop



(b) bridging



(c) CO_3-form

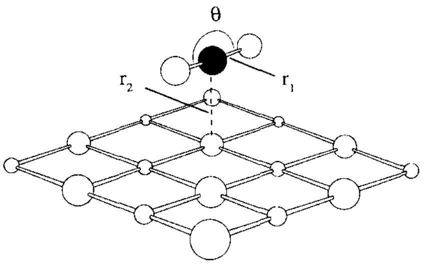


Fig. 2. Schematic representations for three possible adsorption geometries: ontop (a), bridging (b), and CO_3-form (c), respectively for the CO_2 and MgO cluster. r_1, r_2, and θ are the geometrical parameters to be optimized.

face. The model of the MgO cluster is referred to that of Ref. 12, where the Mg_8O_8 cluster is successfully applied to the study of the dissociative adsorption processes of the HCOOH molecule on the MgO(001) surface though the second layer of MgO is not involved explicitly in the calculations. So it would be reasonable to consider only the first layer of MgO as long as the interaction energy is less than or comparable with the dissociative adsorption energy. Further, chemically modified MgO cluster is fixed at its original geometry to mimic the rigid bulk attachment.

We investigated the intermolecular interactions between a CO_2 molecule and the MgO cluster by the Kitaura–Morokuma analysis for the most stable geometry among the above three types of adsorption. Here we have to address the energy decomposition. At first, the total interaction energy ΔE is divided into the deformation energy ΔE_{def} of a CO_2 molecule and the intermolecular interaction energy ΔE_{int} as

$$\Delta E = \Delta E_{\mathrm{def}} + \Delta E_{\mathrm{int}}, \tag{1}$$

since the CO_2 molecule is allowed to change its geometry during the optimization processes. Definitions of ΔE_{def} and ΔE_{int} are schematically illustrated in Fig. 3. It should also be noted that ΔE is expressed by the following equation:

$$\Delta E = E(\mathrm{CO_2} + \mathrm{Mg_8O_8}) - (E(\mathrm{CO_2}) + E(\mathrm{Mg_8O_8})), \tag{2}$$

where $E(\mathrm{CO_2{+}MgO})$, $E(\mathrm{CO_2})$, and $E(\mathrm{MgO})$ are the total energies of the supermolecule, isolated CO_2, and MgO cluster, respectively. The ΔE_{int} in Eq. 1 is further decomposed into several terms based on the Hartree–Fock molecular orbital method as follows:[4]

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{ES}} + \Delta E_{\mathrm{EX}} + \Delta E_{\mathrm{PL}} + \Delta E_{\mathrm{CT}} + \Delta E_{\mathrm{MIX}}. \tag{3}$$

The first term ΔE_{ES} in Eq. 3 is the classical electrostatic interaction i.e. the classical coulombic interaction between two monomers, and the second term ΔE_{EX} is the exchange interaction originating from the quantum chemical method. Both ΔE_{ES} and ΔE_{EX} are the interactions between undistorted monomers. The third term ΔE_{PL} is the energy of the polarization of charge distribution of individual monomers and the fourth interaction ΔE_{CT} is the energy of charge-transfer from one monomer to another and vice versa. The third and fourth terms ΔE_{PL} and ΔE_{CT} are the interactions to which especially we want to pay attention from a point of chemical modifications, because ΔE_{PL} and ΔE_{CT} are closely related to the concepts of chemical hardness and electron negativity of atoms, respectively. The last term ΔE_{MIX} is the energy of the coupling term between the various energy components. The details of each term are given in Ref. 4. Once the values of the energy components are determined, we are ready to choose what elements should be introduced to the surface. If the polarization energy is the dominant component in the total stabilization energy, chemically soft atoms could be candidates for the chemical modifications. In a case when the charge transfer enegy from a CO_2 molecule to the MgO surface is dominant, the introduction of elements that have large electron negativity will give rise to the larger charge transfer energy. The effect of the chemical modification should be examined also by the Morokuma decomposition.

Geometry optimizations are done at the RHF level. The effects of the electron correlation are considered by the RMP2 method with Gaussian 94 ab initio program package.[15] The energy decomposition analysis is performed by the Gamess program package at the RHF levels.[16] Although there may be a possibility of the contamination of higher spin multiple states for the truncated systems, the calculations are done only for the singlet states to mimic infinite systems in accordance with other calculations.[10—12] Through all the

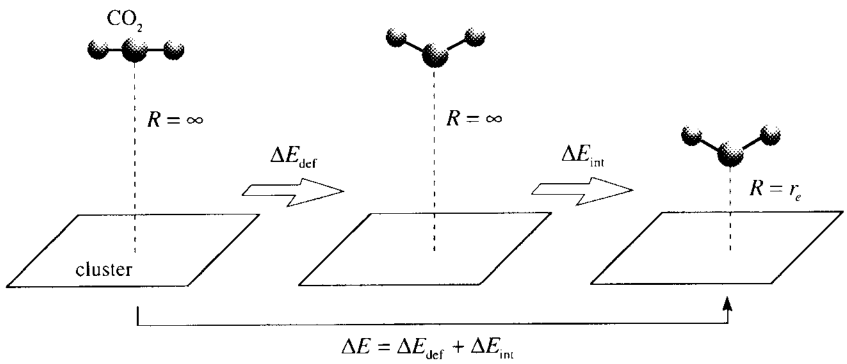


Fig. 3. Relationship between ΔE, ΔE_{def}, and ΔE_{int} is illustrated schematically. ΔE_{def} is defined as a deformation energy of an isolated CO_2 molecule at the adsorption geometry. r_e is the equilibrium intermolecular distance between the cluster and CO_2.

calculations, no symmetry of the electronic state is assumed and Huzinaga's MIDI(321/21) split valence basis sets augmented by polarization functions are employed.[17]

Results and Discussion

Optimized geometrical parameters for the three types of adsorption; ontop, bridging, and CO_3-form are shown in Figs. 4(a), 4(b), and 4(c), respectively. The equilibrium CO distance and OCO angle of an isolated CO_2 molecule are 1.14 Å and 180 degree and these are the initial geometry of the CO_2 molecule for the optimizations. As for the ontop and the bridging type of adsorption, distortion of the CO_2 molecule is not significant, while the CO_3-form gives larger deformation, where the CO bond distance is enlarged to 1.218 Å and the OCO angle is distorted to 135.32 degree. Interaction energies expressed by Eq. 2 for three configurations are also given in Fig. 4. The most favorable type is the CO_3-form. While the experimentally observed adsorption energy of MgO and CO_2 is about 33 kcal mol^{-1} for extremely low CO_2 coverage, it is almost constantly 26 kcal mol^{-1} independent of the coverage.[18] This is in good agreement with the present result of 25.90 kcal mol^{-1} at the most stable adsorption geometry i.e. CO_3-form. The large deformation of the CO_2 molecule can be attributed to the strong interaction between CO_2 and MgO cluster. We performed a Morokuma analysis for this structure to investigate the intermolecular interaction ΔE_{int} in Eq. 1. The results of the decomposition analysis are summarized in Table 1. We summed up the electrostatic interaction ΔE_{ES} and the exchange interaction ΔE_{EX} because both are interactions between undistorted wavefunctions of monomers. We can see that the charge transfer interaction gives the largest contribution to total stabilization energy. Furthermore, the decomposition of the charge transfer energy shows that the charge transfer interaction from MgO cluster to CO_2 molecule is larger than its counterpart. According to Mulliken's population analysis, the net charge of the CO_2 molecule is -0.3821, which also indicates that the negative charge flow from the MgO cluster to the CO_2 molecule occurs. From these results we can understand the chemical nature of the optimized geometry of the CO_3-form.

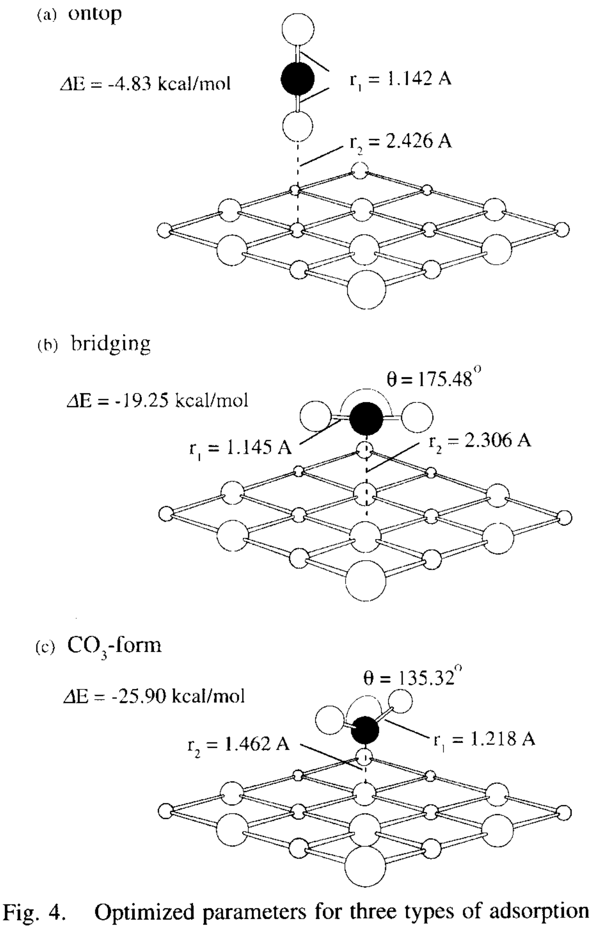


Fig. 4. Optimized parameters for three types of adsorption geometry for CO_2 and Mg_8O_8 cluster.

Table 1. ΔE, ΔE_{def}, ΔE_{int}, in Eq. 1 and Energy Decomposition Analysis of ΔE_{int} for Mg_8O_8–CO_2 System

Interaction (Mg_8O_8–CO_2)	Energy/kcal mol^{-1}
ΔE	−25.90
ΔE_{def}	54.62
ΔE_{int}	−80.52
ΔE_{int}	−80.52
ΔE_{ES+EX}	152.70
ΔE_{POL}	−107.42
ΔE_{CT}	−181.79
$(\Delta E^{CT}_{cluster \rightarrow CO_2})$	−125.92
$(\Delta E^{CT}_{CO_2 \rightarrow cluster})$	−55.87
ΔE_{MIX}	56.06

The electron flow into the carbon atom of the CO_2 molecule will cause the electron repulsion of oxygen atoms of CO_2 and hence the CO bond distance is enlarged and the OCO bond is seriously bent. Here we intend to assist the charge flow from the MgO cluster to CO_2 in order to increase the cohesive energy between the cluster and CO_2. The introduction of atoms that have small electron negativity to the MgO cluster will lower the electron negativity of the whole cluster; therefore, it is expected that the charge transfer from MgO to CO_2 will be enhanced. In this study we replace two Mg atoms by two Ca atoms, since the electron negativity of the Ca atom is 2.2, while that of the Mg atom is 3.75.[19] Simultaneous replacement of *two* Mg atoms is intended to make the effect of the chemical modifications more significant than one atom replacement. Fortunately, the electronic structure change is considered not so serious after the displacement because the Ca atom has the same number of valence electrons as the Mg atom. The positions of the displacement are depicted in Fig. 1, where we performed displacement at positions of $\alpha\beta$, $\gamma\delta$, and $\gamma\varepsilon$. For these three types of displacement, the geometry optimizations are carried out for the CO_3-form structure to determine which type of displacement is favorable for the adsorption. In Table 2, ΔE in Eq. 1 for each type of displacement are given. The displacement of Mg atoms at the positions of $\alpha\beta$ is found to be the most favorable for the adsorption. Furthermore, it should be noted that the ΔE becomes smaller, i.e. the adsorption energy becomes larger, after the displacements. To substantiate the effect of the displacements, the energy decomposition analysis is performed for the $\alpha\beta$ displacement. Table 3 shows the results of the Morokuma analysis for the CO_2 and a $Ca_2Mg_6O_8$ cluster. The most important stabilizing effect is due to the charge transfer interaction. In addition, the increase in ΔE_{int} by the chemical modification can be mainly attributed to the increase in the charge transfer energy. And the decomposition of charge transfer interaction indicates that the negative charge flow from the Ca/MgO cluster to CO_2 increases after the chemical modification. Accordingly the net negative charge of CO_2 increased from −0.3821 to −0.3921. The effects of the displacement of Mg atoms by Ca atoms at the positions of $\alpha\beta$ are summarized in Fig. 5. Electron correlation effects have been verified by RMP2 calculations for the optimized CO_2-cluster complex. The results are summarized in Table 4. The correlation energy is estimated approximately at 10^{-4}—10^{-3} au for Mg_8O_8 and $Ca_2Mg_6O_8$ clusters. The electron correlation must be considered with care; neverthless, it would not give serious effects on the qualitative discussions. The molecular orbital analysis also provides us with the useful information on the mechanism of the enhancement of the charge transfer interaction that is brought about by the chemical modification. In Fig. 6 a schematic picture of the electron donor orbital of MgO cluster (HOMO) is drawn. The cluster HOMO is characterized by the p_z atomic orbitals localized at the O atoms. Because the approach of sp_z atomic orbitals of vacant CO_2 molecular orbital (LUMO) will form a σ-type bridge with the cluster HOMO, the HOMO–LUMO inetraction can be considered

Table 2. Interaction Energy ΔE for Ca Doped MgO Clusters Interaction energy for MgO cluster is also shown as a reference.

Cluster	ΔE/kcal mol^{-1}
Mg_8O_8	−25.90
$Ca_2Mg_6O_8$ ($\alpha\beta$)	−30.23
$Ca_2Mg_6O_8$ ($\gamma\delta$)	−22.70
$Ca_2Mg_6O_8$ ($\gamma\varepsilon$)	−19.50

Table 3. ΔE, ΔE_{def}, ΔE_{int}, in Eq. 1 and Energy Decomposition Analysis of ΔE_{int} for $Ca_2Mg_6O_8$–CO_2 System in Which Two Mg Atoms at α and β Site in Fig. 1 are Replaced by Ca Atoms

Interaction ($Ca_2Mg_6O_8$–CO_2)	Energy/kcal mol^{-1}
ΔE	−30.23
ΔE_{def}	56.63
ΔE_{int}	−86.85
ΔE_{int}	−86.85
ΔE_{ES+EX}	154.08
ΔE_{POL}	−112.12
ΔE_{CT}	−188.38
($\Delta E^{CT}_{cluster \to CO_2}$)	−130.43
($\Delta E^{CT}_{CO_2 \to cluster}$)	−57.94
ΔE_{MIX}	59.57

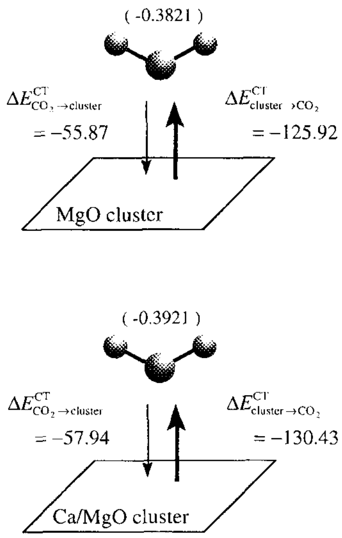


Fig. 5. Comparison of the charge transfer interaction between before and after the chemical modification. The values inside the parenthesis are the Mulliken's electron populations. Units for the energies are kcal mol^{-1}.

Table 4. Total Energies in RHF, UHF, and UMP2 Calculations for CO_2–Mg_8O_8 and CO_2–$Ca_2Mg_6O_8$ Complex

Complex		Energy/a.u.
CO_2–Mg_8O_8	RHF	−2370.560354
	MP2	−2370.561822
CO_2–$Ca_2Mg_6O_8$ ($\alpha\beta$)	RHF	−3321.134185
	MP2	−3321.134261

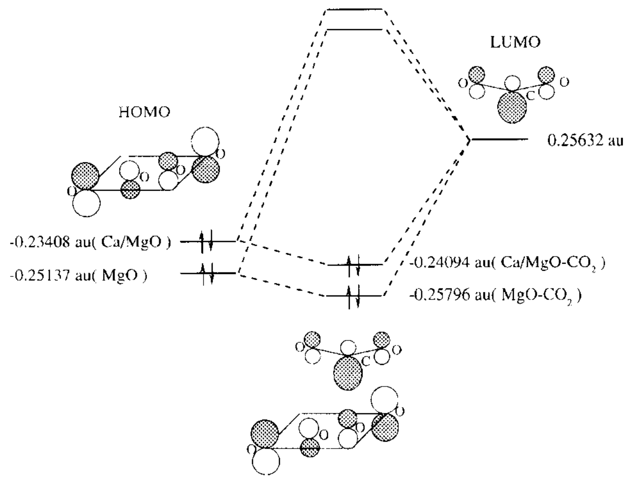


Fig. 6. Schematic picture of the molecular orbital interaction between donor p_z orbital on the four-fold coordinated oxygen atom of MgO cluster and sp_z acceptor orbital on carbon atom of CO_2.

to be the main contribution to the charge transfer energy from the cluster to CO_2. By replacing the Mg atoms by Ca atoms at the positions of $\alpha\beta$, the sum of the square of LCAO coefficients of p_z orbitals of the O atom at the adsorption site increases from 0.01738 to 0.02083, which implies that the HOMO–LUMO overlap is enhanced by the modification. The introduction of Ca atoms also raises the energy level of the cluster HOMO from −0.25137 to −0.23408. It is apparent that the HOMO–LUMO interaction is increased as a consequence of these phenomena. As for the cases of $\gamma\delta$ and $\gamma\varepsilon$ replacements, the sums of the square of LCAO coefficients on O atom are decreased, which gives rise to the decrease of charge transfer interaction energies.

The optimal geometry has been determined by assuming the three possible molecular formations of adsorption by ab initio calculations. The CO_3-form complex is found to be the most stable, where the CO_2 group is strongly bent. The decomposition of the intermolecular interaction for the CO_3-form complex reveals that the charge transfer interaction is the dominant term in the total molecular interaction. For the purpose of increasing the adsorption energy, two Ca atoms have been introduced to accelarate the charge transfer from the MgO cluster to the CO_2 molecule. The effect of the chemical modification has been confirmed by the energy decomposition analysis. The electron donation from the MgO cluster to the CO_2 molecule is realized by the formation of a σ-type electron bridge due to the interaction between MgO HOMO and CO_2 LUMO. Throughout this work we focus our attention on the charge transfer interaction as a key quantity for the chemical modifications; however, the electron polarization effect should be considered in the case when the polarization interaction is dominant among the interaction components. In such a case it would be expected that the introduction of chemically soft elements will be effective.

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