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# Density functional study on the reaction of CO molecules with MgO surfaces

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## Abstract

Adsorption of CO to the MgO surface modeled by $Mg_nO_n$ ($n=4$, 6, 9, 10) clusters was investigated employing the density functional method, and modes of bonding, adsorption energies, and CO exchange mechanisms were discussed. The atoms at the low coordination sites possess the small amount of charges consistent with the crystal field theory. The adsorption to such sites results in large stabilization though the magnitude is less remarkable than in the case of hydrogen adsorption. A possible mechanism for the CO exchange reaction, observed experimentally, is presented based on the energetics calculated. The CO's adsorbed and in the gas phase are exchangeable through the two-molecule adsorption state, which is realized at the edge site or the O-atom defect site. For the latter, the structure of the intermediate is more consistent with the IR measurement.

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## 1. Introduction

CO adsorbs to MgO surfaces usually associatively but causes complicated reactions such as the polymerization and the O-atom exchange as well as simple monomeric adsorption. [1] The theoretical calculation based on the density functional method was applied to investigate the MgO/CO surface interactions using several cluster models of $Mg_nO_n$ ($n=4$, 6, 9, and 10). The stable structures of adsorbate and the mode of bonding were discussed. Attention is also paid to elucidate the mechanisms of the exchange between adsorbed CO and CO in the gas phase. Ito et al. proposed the mechanism of CO exchange reaction as illustrated in Fig. 1 based on their TPD and IR measurements. [2] CO is adsorbed to the Mg and O atoms in the bridge or chain form, and this species is labeled as $K_1$. Another CO is adsorbed to the same Mg atom and the species with a twin configuration is formed. This twin species converts to $K_0$ and $K_1'$ species. Then there

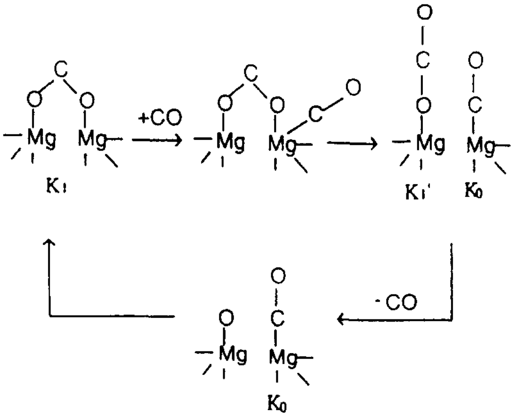

Fig. 1. Proposed reaction scheme for CO exchange reaction on the MgO surface.

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are two possibilities for one-molecule desorption. When the $K_0$ species desorbs, the reaction simply proceeds backward, whereas on removing $K_1'$ species, $K_0$ converts to the more stable $K_1$. Thus this reaction scheme explains the exchange of CO during adsorption–desorption cycle.

## 2. Models and calculation method

The model clusters employed in this work are classified into two groups. One is the $Mg_4O_4$ cube and its assembled form, $Mg_nO_n$ ($n=4$, 6 and 9). We call these the *convex* model. This model was used to examine the difference in interactions among the sites and the bonding modes. The other group of clusters, $Mg_nO_n$ ($n=9$ and 10) represents the O-atom defect site in the polar (111) facet, which is called the concave model. To represent the environment of the cluster surrounded by the bulk atoms, the clusters are embedded in the 'sea' of point charges. In the geometry optimization, the internal structure and orientation of CO were optimized for the convex models. For the concave models, the location of a few surface O atoms close to CO was also optimized. After the structures were optimized at the local potential level, the total energy was estimated by a single point calculation including the non-local correction.

The program deMon was used with implementation of the point charge and the internal coordinate optimization scheme. [3]

## 3. Results and discussion

### 3.1. Adsorption modes

For single molecule adsorption, the difference among the coordination numbers was examined with the convex clusters, $Mg_nO_n$ ($n=4$, 6 and 9).

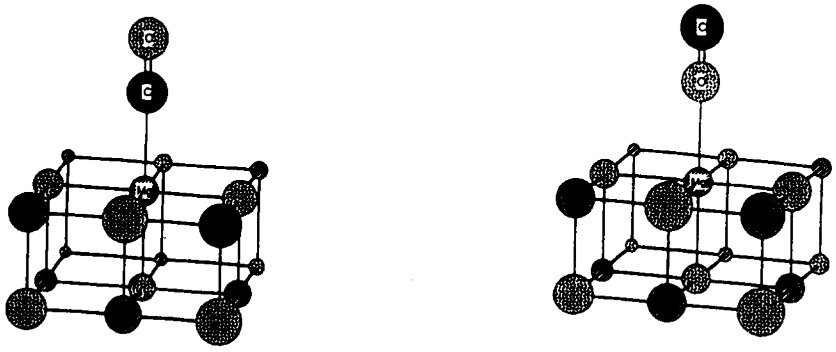

Fig. 2. C-end and O-end adsorption of CO to $Mg_9O_9$ cluster.

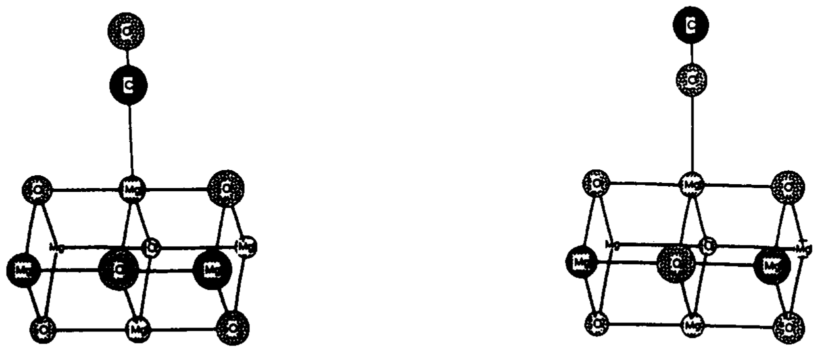

Fig. 3. C-end and O-end adsorption of CO to $Mg_6O_6$ cluster.

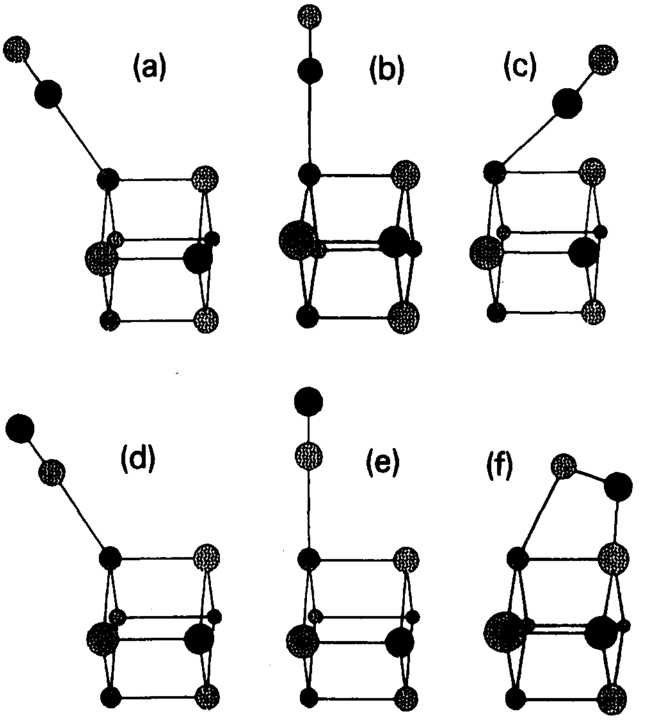

Fig. 4. C-end ((a) to (c)) and O-end ((d) to (f)) adsorption of CO to $Mg_4O_4$ cluster. (a) Linear, (b) intermediate, (c) bridge, (d) linear, (e) intermediate, and (f) chain.

Table 1
Adsorption energy of CO molecule on different coordination number sites (kcal/mol)

| | C-end | O-end |
|---|---|---|
| $Mg_9O_9$ | 11.7 | 10.9 |
| $Mg_6O_6$ | 17.4 | 13.9 |
| $Mg_4O_4$ (linear) | 19.0 | 12.8 |
| $Mg_4O_4$ (intermediate) | 20.6 | 7.3 |
| $Mg_4O_4$ (bridge/chain) | 21.9 | 19.9 |

Table 2
Mulliken charge of atoms on $Mg_9O_9$ cluster

| | Mg | O |
|---|---|---|
| $Mg_9O_9$ (5c) | +1.39 | −1.29 |
| $Mg_9O_9$ (4c) | +1.20 | −1.19 |
| $Mg_9O_9$ (3c) | +1.06 | −1.09 |

The configurations of adsorbed CO are shown in Figs. 2–4, and the calculated adsorption energies in Table 1. CO is stably adsorbed to the Mg atom at either the C or O end. Table 1 shows that the adsorption energy increases with decrease in the coordination number of the Mg atom. This trend is consistent with other calculations. [4] However, it is not so remarkable compared with the $MgO/H_2$ system, where the H atoms did not bind to the surface atoms at the 4- and 5-coordination sites. [5] The charge on atoms in the free cluster is shown in Table 2. As expected from the crystal field theory, the atoms at the low coordination number site possess only a small amount of charge.

The configurations of CO are investigated in detail for the $Mg_4O_4$ cluster. In the Mg–CO configuration, the energy continuously lowers from the linear to bridged form, whereas there is a small barrier between the linear and chain forms for the Mg–OC configuration. Adsorption to the surface O atom is also examined and found to be unstable in both O–CO and O–OC configurations. When the second CO is adsorbed to the bridge form (see Fig. 4c and Fig. 5a), the resulting structure and its optimized structure are shown in Fig. 5b and c, called the twin and twin-opt. forms, respectively.

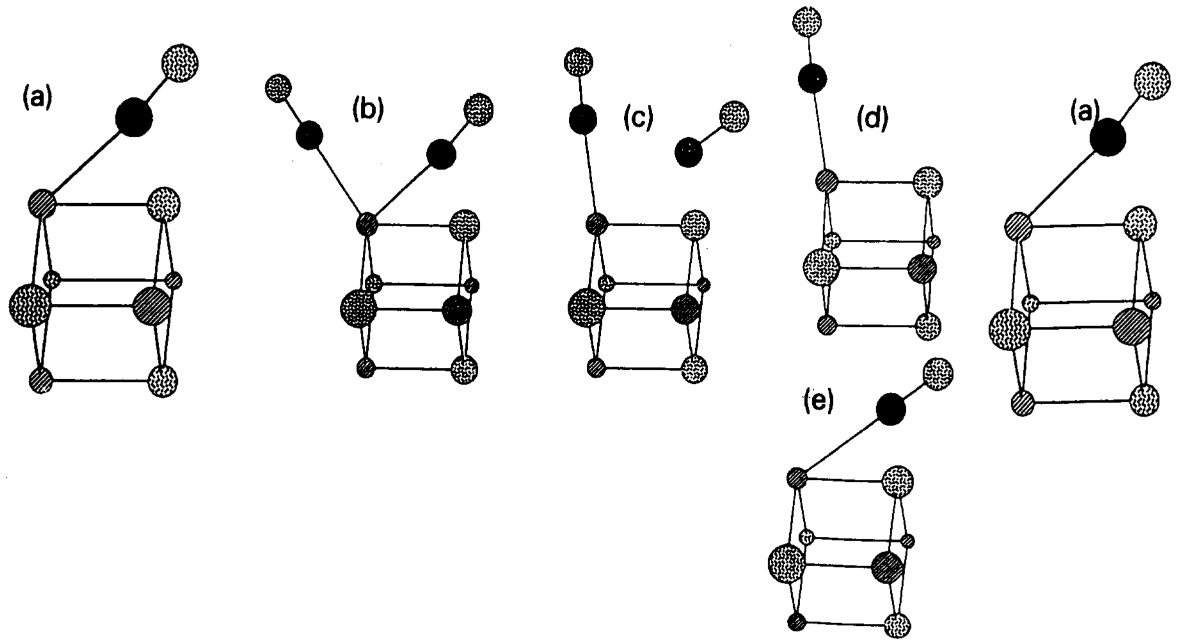

Fig. 5. The edge–corner site mechanism for CO exchange reaction. (a) Bridge (21.9), (b) twin (38.0), (c) twin-opt. (39.6), (d) CO-left (21.0), and (e) CO-right (21.3). The value in parentheses is the adsorption energy in kcal/mol.

In these configurations, one CO is adsorbed to the Mg atom in linear form and the other is bridging to the Mg and O atoms. Thus the interactions with the surface O atom become stable only in the co-adsorption to the adjacent Mg atom.

The influences of cluster size and coordination number are discussed using the $Mg_6O_6$ cluster. The four stable configurations of adsorbed CO are shown in Fig. 6. The adsorption energies, which are cited in the caption of Fig. 6, are compared with those for the $Mg_4O_4$ cluster. In the configurations Fig. 6a and c, where the Mg atom is in the (3c) site, the adsorption energy increases by 2–3 kcal/mol more than that for the $Mg_4O_4$ cluster. This increase is ascribed to the formation of weak O–Mg or C–Mg bonding interactions in the larger cluster. On the other hand, the adsorption energy decreases for configurations Fig. 6b and d, possibly due to the change in the coordination number of bonded Mg atom from (3c) to (4c). Thus the coordination number dependence is not negligible, but it is much smaller than in the case of hydrogen adsorption.

Table 3 shows the charges on C and O atoms in CO adsorbed to the $Mg_4O_4$ cluster. In the C-end adsorption to the Mg atom (linear (C-end)), the polarization within CO is found to be very small. In the bridge form, the C atom comes close to the surface O atom, and the polarization and the charge transfer to CO increase. For the O-end adsorption, the polar Mg–O bond formation further enhances the polarization. So the magnitude of charge is largest for the chain form. This idea is confirmed again in the twin-opt. form: the polarization is higher for the bridge-type CO. We can expect that the ionic character is increased in the bonding between the charged-up atoms.

### 3.2. CO exchange reaction

A possible mechanism for the CO exchange is proposed based on the above results. Starting from the bridge form, the second CO adsorption leads to the twin-opt. form through the twin form. The adsorption energy for each configuration is also shown in Fig. 5. Then the desorption energy for the right and left side CO's are calculated to be

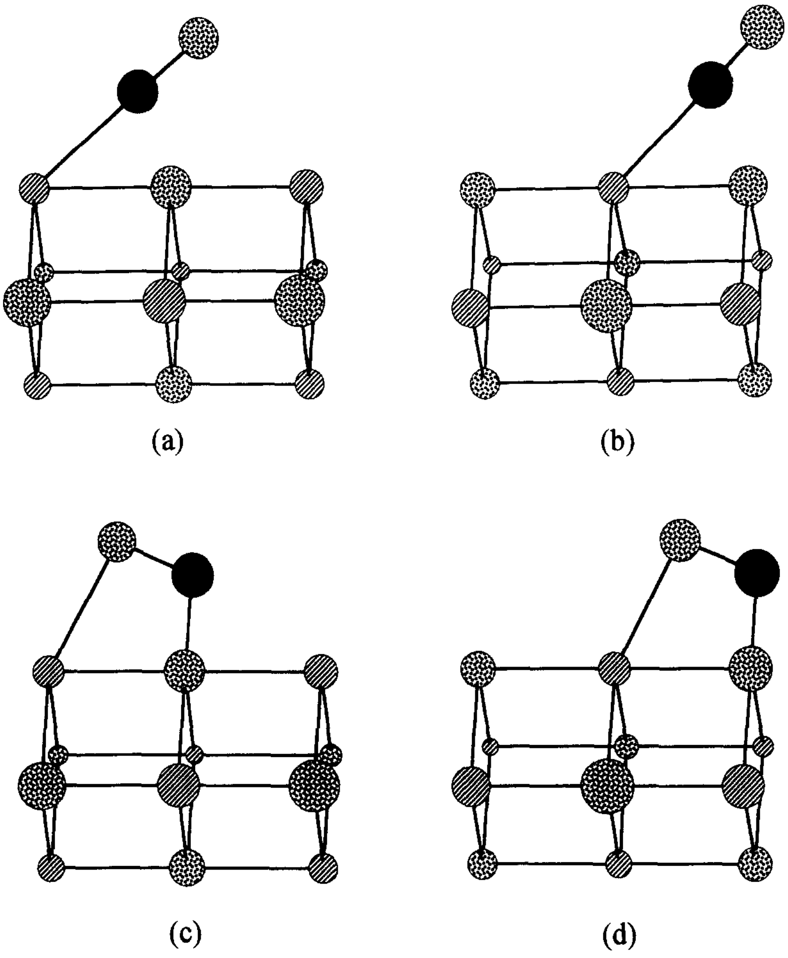

Fig. 6. Four stable configurations of CO adsorbed to $Mg_6O_6$ cluster. (a) Linear Mg(3c) (24.0), (b) linear Mg(4c) (20.0), (c) chain Mg(3c) (22.9), (d) chain Mg(4c) (14.0). The value in parentheses is the adsorption energy in kcal/mol.

18.6 and 18.3 kcal/mol, respectively. Almost the same value of the energy means almost the same probability for desorption of CO. Both desorbed configurations (shown in Fig. 5d and e) reproduce the bridge form (Fig. 5a) by further optimization. So a single adsorption–desorption cycle can replace half the adsorbed CO with that in the gas phase, which explains the exchange reaction observed experimentally. [2]

Table 3
Mulliken charge on atoms in CO adsorbed to $Mg_4O_4$ cluster

| | C-end | O-end |
|---|---|---|
| Linear (C-end) | ~0.0 | −0.03 |
| Bridge (C-end) | +0.13 | −0.25 |
| Linear (O-end) | +0.27 | −0.25 |
| Chain (O-end) | +0.37 | −0.44 |
| Twin-opt. (linear) | −0.09 | −0.08 |
| Twin-opt. (bridge) | +0.15 | −0.25 |

However, the FT-IR measurement has indicated that the two C–O bonds must be in an equivalent environment. [2] Although in the twin and twin-opt. forms, the C atom in the right hand CO comes close to the surface O atom, the nature of two C–O bonds is not equivalent: One of them remains as the internal C–O bond and the other is the bonding with the surface O atom. This leads to the assumption that the surface defect sites model could be more suitable than the edge–corner site model. We employed three kinds of clusters, $Mg_9O_9$, $Mg_9O_9H$, and $Mg_{10}O_{10}$. The $Mg_9O_9$ cluster represents the (111) facet composed of the

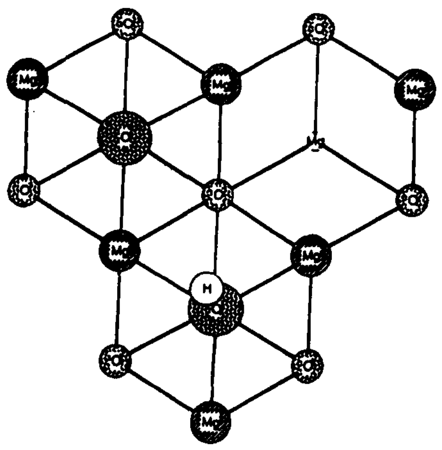

Fig. 7. Structure of $Mg_9O_9H$ cluster model.

three three-coordinated (3c) O atoms but one O atom is removed to simulate the O atom vacancy. In the $Mg_9O_9H$ cluster, a H atom is adsorbed to one of the (3c) O atoms to block that site. The free $Mg_9O_9H$ cluster is illustrated in Fig. 7, and the structure of $Mg_9O_9$ is exactly the same as $Mg_9O_9H$ except for the H atom. The $Mg_{10}O_{10}$ cluster is also used since it has one (3c) O atom on the surface (Fig. 8a).

The adsorbed CO is caught by the vacancy and forms the bridged symmetrical O–C–O structure with the surface O atom (Fig. 8b). Since the two O atoms in the O–C–O structure are completely equivalent, this intermediate is also a candidate for the O atom exchange with the surface. The adsorption energy is calculated to be 79 kcal/mol. This relatively large value seems to be reasonable for the binding at the vacancy site. Using the $Mg_9O_9$ cluster, CO forms the carbonate-like species with much larger adsorption energy. However, $CO_3$-like species is not supported by the IR measurement. The calculation with the $Mg_9O_9H$ cluster again results in the O–C–O species, and the adsorption energy is smallest of the three. So this type of blocking is necessary to be consistent with the experiment. We understand that the site modeled by the $Mg_9O_9$ cluster is too active to exist stably in the realistic surfaces. Any species may adsorb and block it.

On adsorption of the second CO molecule, the adsorption energy amounts to 103 kcal/mol for

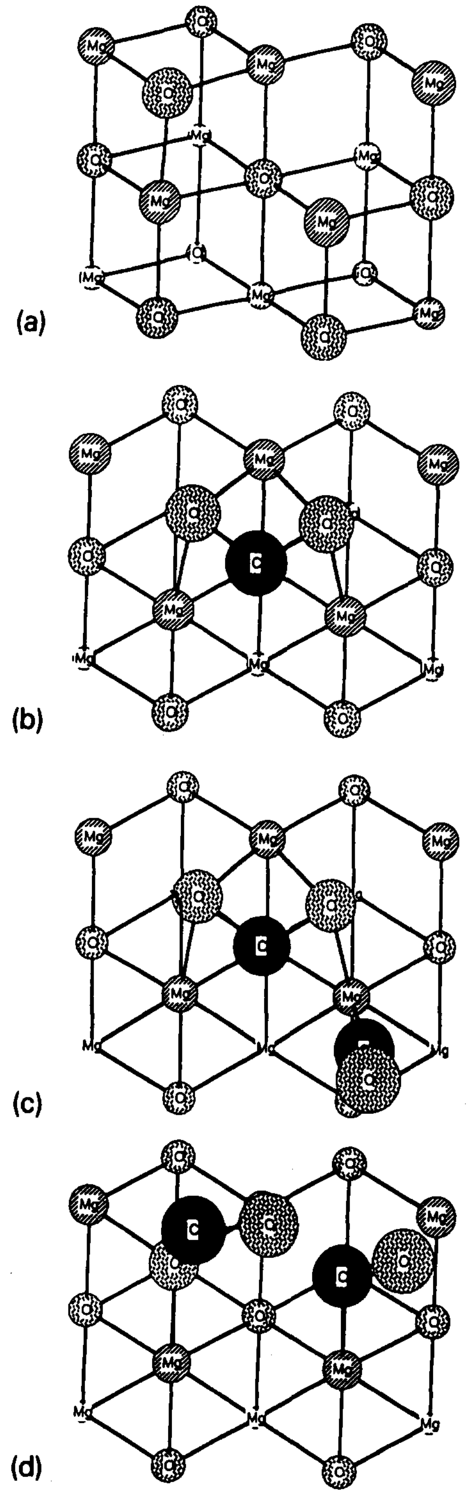

Fig. 8. The defect site mechanism for CO exchange reaction. (a) $Mg_{10}O_{10}$ free cluster; (b) single CO adsorbed structure, OCO form; (c) two CO adsorbed structure; (d) structure after relaxation of (c).

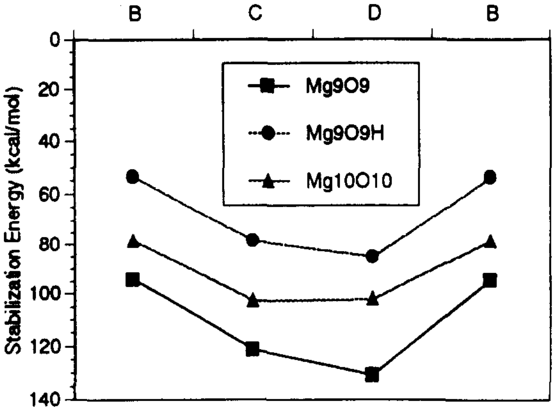

Fig. 9. Change in stabilization energies for $Mg_9O_9$, $Mg_9O_9H$, and $Mg_{10}O_{10}$ clusters along the cycle of configurations (b), (c), (d), and (b) shown in Fig. 8.

two CO's (Fig. 8c). The change in adsorption energy is shown by the curves in Fig. 9. Further rearrangement causes the first CO to move from the symmetrical position to the left side (Fig. 8d), and the C atom of the second CO goes into the vacancy. Desorbing the first CO, the second CO reproduces the symmetrical O–C–O structure shown in Fig. 8b). This means that the symmetrical structure is a key structure for this exchange reaction and also for the O atom exchange with the lattice oxygen. The successive adsorption–desorption cycle replaces half the amount of adsorbed CO, which is confirmed by the TPD experiments using the oxygen isotopes. Thus we have presented the two models of the CO exchange reaction. The edge–corner model can explain the essential part of the reaction except for the IR data. On the other hand, too large a stabilization energy is a demerit for the defect site models. This implies the difficult aspect in modeling the defect sites. For taking account of the relaxation of lattice atoms more completely, we must use still larger clusters. Another interpretation for the present result is that the O–C–O species may be an inactive intermediate: this species is a stable and observable subject for spectroscopy but may not be the active intermediate for the exchange reaction.

## 4. Conclusion

In this work we have examined the interactions of the CO molecule with MgO surfaces, and presented possible mechanisms for the adsorbed and gas phase CO exchange reaction. The following information is drawn from our calculations.

Adsorption and bonding:

(1) CO is adsorbed to the Mg atom with either C- or O-end, but not to the O atom.

(2) Adsorption to the O atom is possible only when the adjacent Mg site is occupied by CO, i.e., in the case of two molecule adsorption.

(3) The calculated Mulliken charge follows a simple rule: atoms with the lower coordination numbers possess the smaller magnitude of charge.

(4) The adsorption is stable for all the (5c), (4c), and (3c) sites, and the stabilization increases in this order. The difference between sites is less remarkable compared to $MgO/H_2$ system.

(5) A larger contribution of the ionic bonding for the CO–surface O atom bonding rather than the CO–Mg atom bonding is observed.

(6) The adsorption energy for the second CO is smaller than for the first CO. (Opposite to the $MgO/H_2$ system.)

CO exchange:

(7) The CO exchange reaction can be explained through the twin configuration on the corner sites.

(8) Another mechanism with a lattice defect site is also possible with much larger adsorption energies. The structure of adsorbed CO is more consistent with the IR data, but it may be an inactive intermediate.

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