Comparative study of oxygen double exchange between O_2 adsorbate and alkaline-earth oxides

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Thermal desorption of doubly exchanged oxygen molecules at temperatures above 800 K is observed not from MgO but from CaO and SrO powders after ¹⁸O₂-gas exposure at room temperature. The exchange reaction was investigated using *ab initio* molecular-orbital calculations. The defective (111) surface clusters of CaO and SrO were found to prepare anion-charged reactive centers to accept the O₂ adsorbate. The adsorbate was incorporated into a key O₅-charged intermediate which can provide an oxygen molecule composed of two lattice atoms for desorption. The nonreactive character of the MgO surface in the ground state is ascribed to the presence of oxygen ions bound strongly at the lattice points. [S0163-1829(96)04344-5]

I. INTRODUCTION

The role of lattice versus adsorbed oxygen atoms has recently become a subject of great interest in various systems, e.g., the oxidative coupling of methane over oxide surfaces,^{1,2} the surface exchange kinetics during oxygen permeation through oxides,³ and surface characterization of ZrTiO₄ by photoassisted exchange.⁴ On the other hand, systematic comparisons of the role of adsorbates on alkalineearth oxides appears to be rather few. In order to obtain insight into the surface-adsorbate interaction, theoretical studies have been made.^{5,6} However, they are mostly restricted to interactions and reactions on MgO surfaces.

So far we have serially studied oxygen exchange on MgO⁷, CaO⁸, and now SrO through thermal-desorption (TD) gas analysis and theoretical analysis of the process using a cluster model geometry-optimization with ab initio molecular orbitals (MO's). In this family of oxides, crystals have wider nearest-neighbor distances in the order of MgO, CaO, and SrO (2.10, 2.40, and 2.58 Å, respectively). One can then expect an easier formation of relaxed local surface structures; they might interact with gas molecules to form intermediates for the exchange on the oxides with the same order (MgO <CaO<SrO). However, here we find a much more dramatic result; the oxygen double exchange at high temperatures (>800 K) does not take place on MgO, while it does occur on CaO and most significantly on SrO. In our previous work, α and β peaks below 600 K were analyzed in detail.⁸ However, the most significant peak (γ) of the doubly exchanged oxygen observed at higher temperatures is entirely unresolved, to our knowledge. In this paper, we present the experimental results of the TD analysis of exchanged O₂ on the SrO surface, and an extended MO analysis of the process on MgO, CaO, and SrO surfaces. This systematic comparison led us to a plausible mechanism of the oxygen double exchange on CaO and SrO surfaces at high temperatures. We further discuss the reason for which a similar hightemperature peak was observed from UV-irradiated MgO.

II. EXPERIMENT

A SrO powder was prepared by the thermal decomposition of Sr carbonate ("Specpure" grade from Johnson Matthey Chem., Ltd.) in a 4-mm-diameter quartz tube. The powder sample was slowly heated to 1170 K and kept for 5 h under high vacuum. This procedure seemed to be sufficient to completely decompose the carbonate.9 After baking, the base pressure was less than 8×10^{-9} Torr. The desorption gas was analyzed by using a quadrupole mass spectrometer (ULVAC, MSQ-400). After being cooled to room temperature (RT), the sample was exposed to isotopically labeled ¹⁸O₂ gas (99 at. % purity, ICON, U.S.A.) for a specified time with an exposure range of $10^2 - 10^4$ L (1 L= 10^{-6} Torr s) through a variable leak valve in the dark. Thermal desorption (TD) was measured up to 1100 K with a linear heating rate of 0.5 K/s. After several cycles of exposure and TD, all the TD curves of ${}^{18}O_2$, ${}^{16}O^{18}O_2$, and ${}^{16}O_2$ become reproducible, which may be due to the disappearance of transient active sites. Hereafter, the reversible adsorption-desorption phenomena will be discussed.

The TD of ${}^{18}O_2$, ${}^{16}O^{18}O$, and ${}^{16}O_2$ on the SrO powder after ¹⁸O₂ exposure of 2000 L at RT are shown in Fig. 1. The TD curves from CaO and MgO powders after ¹⁸O₂ adsorption, which were taken from Refs. 8 and 7, are also shown in the inset of the figure. Here the exposure conditions were the same (2000 L at RT), and TD intensities were measured with the normalized mole amount for three oxides.

For SrO powders, TD peaks are observed at 375-570 K (peaks β_1 and β_2) and 915 K (γ). The β and γ peak notations correspond to those previously used for CaO/O₂ for convenience.⁸ Peak β_1 consists of ¹⁶O¹⁸O and ¹⁶O₂ with a small amount of ¹⁸O₂, and peak β_2 at about 530–570 K consists mainly of ¹⁶O¹⁸O and ¹⁶O₂. Peak γ consists of ¹⁶O₂ with a small amount of ¹⁶O¹⁸O. Thus, single- and double-oxygen exchanges (peaks β_1 , β_2 , and γ , respectively) take place on the surfaces. All of the TD peak heights increased linearly with the exposure, and were not saturated even at high exposure (\sim 7000 L). No TD's of CO and CO₂ were observed in the temperature range examined, indicating that carbon contamination was absent on the SrO surfaces. Similar exchange features are observed for ¹⁸O₂-adsorbed CaO powders.⁸ For SrO and CaO surfaces, the γ peaks are the largest. However, for MgO, no ${}^{16}O_2$ TD (peak γ) was observed (in the inset of Fig. 1) except for the case when UV preirradiation was done.⁷ This indicates that no active sites for double-exchange exist on unexcited MgO surfaces. By analyzing the initial rise of the partial pressure, activation energies for desorption $(E_d's)$ of peak γ were roughly esti-

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FIG. 1. TD curves of $^{18}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{16}\text{O}_2$ gases after 2000-L exposure to $^{18}\text{O}_2$ at room temperature of SrO powder baked at 1170 K. Those for MgO and CaO powders reported in Refs. 7 and 8, respectively, are shown in the inset.

mated to be 1.4 and 1.6 eV for the CaO and SrO powders, respectively.

III. CLUSTER MODELS AND COMPUTATIONAL METHODS

We have previously shown that a single O ion and a relaxed O_2 site on a (111) cation surface of CaO can explain the single and double exchanges on the oxide, respectively.⁸ Due to the energetic equality of key intermediates, this mechanism has been applicable only to the low-temperature peaks where desorption of both singly and doubly exchanged O_2 molecules takes place. We will propose different active sites on the (111) surfaces for the high-temperature exchange. Since the (111) surfaces are known to be thermally faceted into sets of the (100) faces, the (111) surfaces as defective corners of the microcrystallites with (100) faces are thought to be distributed. Our model is shown in Fig. 2 based on this hypothesis.

Ab initio geometry optimizations are carried out for the $M_{10}O_8$ (M = Mg, Ca, and Sr), and Ca₁₀O₁₀ clusters using the GAUSSIAN 92 program.¹⁰ The basis set used for the optimizations is LANL1MB (Ref. 11) for the Hartree-Fock wave functions implemented in the GAUSSIAN 92 program. After they are completed, single-point energy calculations of those clusters were made with the LANL1DZ (Ref. 11) basis set embedded on 470 point-charge centers (Fig. 2). Net charges of these centers were taken to be $\pm 0.305e$, which were derived



FIG. 2. A cluster model of the CaO surface. Ten calcium and eight oxygen atoms are explicitly considered in the molecular-orbital calculations, and are numbered. 470 point-charge centers (charge= ± 0.305) are embedded on the Ca₁₀O₈ moiety. All the Ca-O distances are taken to be 2.405 Å. Not all of the backside charge centers are shown for clarity.

from Mulliken atomic charges of the Ca₁₀O₈ cluster with the LANL1DZ basis set. All the molecular-orbital calculations were performed on a CONVEX C-220 computer at the Information Processing Center (Nara University of Education). The energy gaps between the conduction and valence bands of the Mg₁₀O₈, Ca₁₀O₈ and Sr₁₀O₈ clusters without geometric relaxation were determined to be 5.6, 4.6, and 4.2 eV, respectively, which are consistent with the observed bulk energy-band gaps (7.7-7.8, 6.8-7.1, and 5.8-6.0 eV, respectively).¹² The discrepancy between the obtained band gaps and the observed bulk ones is generated by terminal effects of the clusters modeling defective corners, and not by any inaccuracy in the computational method. This is, in fact, confirmed by calculating a bulk-type Sr₁₄O₁₄ cluster with 698 point charges. The large model is found to give a gap of 6.0 eV, which is satisfactorily in the experimental range of 5.8-6.0 eV.12

Here single point defects on flat (001) surfaces are not taken into consideration. This is because their inactivity is well established. For example, a CO attack on an F_s center (anion vacancy) on the MgO (001) surface leads to a very small binding energy, while the attack on a V_s center (cation vacancy) yields only CO doping.¹³ The sites including coordinatively unsaturated oxygen ion pairs are operative for the rolling double-exchange mechanism of CO₂ on MgO, i.e., $C^{16}O_2$ TD is observed after $C^{18}O_2$ adsorption.¹⁴ Thus the surface cluster containing nearby oxygen atoms in Fig. 2 may be a candidate for the double exchange.

IV. RESULTS OF CALCULATIONS AND DISCUSSION

Figure 3 displays the obtained O_2 exchange process $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow F$ on the $Ca_{10}O_8$ cluster. At state *A*, the positions of three oxygen atoms O(2), O(9), and O(11) are confirmed to be nearly at their lattice points. To initiate



FIG. 3. Geometries of the O₂ adsorbed and desorbed clusters. Models *A*, *B*, and *F* are of Ca₁₀O₈ and are of geometries with optimized positions of O(2), O(9), and O(11). Models *C*, *D*, and *E* are of Ca₁₀O₁₀ and are of geometries with optimized positions of O(2), O(9), O(11), O(19), and O(20). Distances between nonoptimized lattice oxygen and calcium atoms are fixed at 2.405 Å. Δe and ΔE are the stabilizing (<0) and destabilizing energy (>0) in eV relative to e(A) and E(C), respectively. Numbers attached to atoms are atomic electronic charges (positive and cationic). Important distances in Å are shown below. O(2)-O(11)=1.404, O(2)-O(12)=1.416, and O(9)-O(11)=2.703 in model *B*. O(19)-O(20)=1.222, O(20)-Ca(3)=2.189, O(2)-O(11)=1.401, and O(2)-O(12)=1.420 in model *C*. O(2)-O(11)=1.390, O(11)-O(20)=1.403, O(19)-O(20)=1.397, and O(9)-O(19)=1.400 in model *D*. O(19)-O(20)=1.397, O(9)-O(19)=1.397, Ca(1)-O(2)=2.133, and O(2)-O(11)=1.220 in model *E*. O(19)-O(20)=1.396, O(9)-O(19)=1.376, and Ca(1)-O(20)=2.117 in model *F*.

the double exchange, however, a distorted surface is needed. State *B* is then found. Three oxygen atoms O(2), O(11), and O(12) are linked like an ozone molecule. This "ozone" molecule is also bound by two calcium ions Ca(1) and Ca(5). Site O(11) in state *A* is now a charged vacancy $[O_v(11)]$ neighbored by the pair of O(2) and O(11). The site can trap an attacking O₂ adsorbate.

After that geometrical relaxation, the adsorbate O(19)-O(20) may be bounded on the Ca₃ triangle. This state *C* represents a physisorption, because the O-O distance of 1.222 Å of the adsorbate is almost the same as that of 1.207 Å in the free oxygen molecule. There are various other energy minima of O₂-trapped structures than state *C*. Some of them are artificial potential wells due to the limited-size cluster. Others correspond to adsorbed states which cannot be related to double exchanges. Geometries with an oxygen atom captured at a lattice point are also present but are not pertinent to the exchanges.

When the adsorbate in state *C* moves to the left, it is trapped and forms a bridge structure of five oxygen atoms in state *D*. State *D* is stable due to the chemisorption. It involves an O₅ intermediate species stabilized by four lattice calcium ions Ca(1), Ca(3), Ca(5), and Ca(17). In the O₅ chain, one terminal oxygen ion O(9) is located nearly at the lattice point. The other terminal one O(2) is not at the lattice one and is mobile. When the O₅ chain is twisted by the supply of thermal energy and the O(20) atom is caught by Ca(1) and Ca(5) ions, an oxygen molecule O(2)-O(11) is driven out. Another physisorption state *E* is then created. The isomerization process $C \rightarrow D \rightarrow E$ is a change of one physisorption—chemisorption—another physisorption. Through the O(2)-O(11) elimination, a stable cluster structure of state *F* is attained. State *F* involves the O₃ (ozone) species. An O₂ double-exchange $O(19)-O(20) \rightarrow O(2)-O(11)$ mechanism has been described. At the cluster side, an ozone intermediate O(11)-O(2)-O(12) in state *B* has been transformed to that O(20)-O(19)-O(9) in state *F*.

While the process is exothermic and appears to be ready, there are two steps which require activation energies. One is the $A \rightarrow B$ step that forms the ozone intermediate via lattice distortions. The other is the $D \rightarrow E$ step to push out the O(2)-O(11) species. The γ peak appears due to the pushing out. Now we notice that the energy changes ΔE 's obtained here are fortuitously consistent with the observed desorption energies (E_d 's, $1.4 \sim 1.6$ eV), although the cluster models used are small. The backward reaction $D \rightarrow C \rightarrow B$ is unlikely due to the energy difference value of $\Delta E = -1.30$ eV in state D (state C is much less stable than state D). The irreversibility of the process seems to correspond to the absence of ${}^{18}O_2$ desorption upon heating in Fig. 1.

We will now discuss why the mechanism is most probable on SrO and almost impossible on MgO. We find that the γ peaks of CaO and SrO appear in almost the same temperature range (800–1000 K) as shown in Fig. 1. Also, we note that the γ peak temperature in UV-irradiated MgO is in the same range. The similarity of γ peak positions suggests that thermal energies are consumed to cleave the O(11)-O(20) covalent bond in state *D*. It is then understandable that the $D \rightarrow E$ (distortion of the O₅ chain) step is rather insensitive to the kind of alkaline-earth oxides. However, the difference in the γ yields among the three oxides is remarkable (27, 8.7, and 0 in arb. units in Fig. 1). The key step then seems to be $A \rightarrow B$, for which the activation energy is very sensitive to the three oxide types. The SrO surface gives the distorted



FIG. 4. *B*-type geometries of four distorted $M_{10}O_8$ clusters (M = Mg, Ca, and Sr), where state *B* is defined in Fig. 3. The geometry of Ca₁₀O₈ is the same as that in Fig. 3. The positions of the three oxygen atoms, O(9), O(2), and O(11), are optimized. The fixed Mg-O, Ca-O, and Sr-O lattice distances are 2.107, 2.405, and 2.580 Å, respectively.

structure, state *B*, more readily than the CaO one.

Figure 4 shows the state *B* geometries. The Ca₁₀O₈ geometry is taken from Fig. 3. Using various initial geometries, we tried to determine state *B* of the Mg₁₀O₈ cluster. This trial led us to two irrelevant geometric isomers (a) and (b). The artificial isomer (a) comes from displacement of O(11) (in Fig. 3-A) to O(2) in Fig. 4(a) leaving O_v(11). The isomer (b) is similar to state *F* in Fig. 3. Both models cannot be con-

cerned with O₂ acceptance. The MgO surface tends to retain at least one oxygen ion at the lattice point even during the formation of O₃ intermediates. In other words, the O₂-like intermediate is rigidly positioned on the MgO surface. In contrast to the inflexible surface cluster Mg₁₀O₈, Ca₁₀O₈ and Sr₁₀O₈ clusters are able to be precursors for the O₅-bridge-type O₂ adsorption. "Soft" alkaline-earth ions are required to cause the process $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow F$.

While the difference in cohesive energies or melting points is small among the three oxides, cation electronic polarizabilities (α) significantly differ in the series Sr²⁺, Ca²⁺, and Mg²⁺ (1.6, 1.1, and 0.094, respectively, in units of 10⁻²⁴ cm²).¹⁵ This trend is very similar to that of the change in γ yields. The larger magnitude of α arises from the interaction of electron orbitals of higher energies (e.g., *d* orbitals in Sr²⁺). This interaction should be larger for the narrower band gap in accordance with its order (SrO>CaO>MgO). In the MgO case, UV irradiation results in electron trapping at surface anion vacant sites to form *F*-type centers, which may then increase the α of Mg ions around reactive sites through contributions of higher-energy orbitals. It is then understandable that peak γ occurs in UV-irradiated MgO. The γ peak yield depends on the cation polarizability.

V. CONCLUDING REMARKS

We have shown in this work that the significant TD peak (γ) of the doubly exchanged O₂ molecule appears at temperatures >800 K on CaO and SrO surfaces but not on MgO. A cluster $Ca_{10}O_8$ model has been used to simulate the exchange process. A reactive precursor, state B, has been found via distortion and formation of an O₃ intermediate. An O₂ molecule is trapped during physisorption (state C), and subsequently is incorporated into the O₅ chain in the key intermediate (state D). Its geometric isomerization drives out an O_2 molecule. After this desorption, a surface with another O_3 intermediate (state F) is generated. The double-oxygen exchange for the peak γ has been described as reorganization of the O_5 intermediate to the O_3 one. The reactive precursor (state B) can not be allowed in the MgO cluster due to its rigid coordination character. Thermal energies seem to be needed for the geometric distortion $A \rightarrow B$. This distortion is easier on SrO than on CaO, which leads to the larger yield of the γ peak on the former surface.

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