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Activation Energies to Characterize Ease of Removal of Various Kinds of Oxygen from Bismuth Molybdate

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The technique of minimum energy paths is used on oxygen ions of different types leaving a unit cell on the surface of the lattice of the 2 : 1 bismuth molybdate (Bi_2MoO_6). Several kinds of behavior are obtained. Oxygen ions originally between the molybdenum and the bismuth layers of the unit cell are first considered. The activation energy computed for the transition of such ions from inside the lattice to outside, near the interface, is approximately 2 eV. This implies that it is possible for some of this type of ion to be removed from the lattice. The corresponding activation energy for an ion in the molybdenum layer is a little larger. For an O^{2-} ion in the bismuth layer, the activation energy is found to be enormously high, apparently implying that such ions could never directly leave the lattice. However, a great deal of information indicates that it is just such an ion that takes part in a chemical reaction with the hydrocarbon. While the presence of the hydrocarbon will perhaps facilitate the removal of this O^{2-} ion by factors not considered in the present analysis, the requirement still seems overly high. It is suggested that the presence of anion vacancies reduces this activation energy. The role of prereduction in forming a reproducible catalyst is hypothesized in this manner.

INTRODUCTION

Many partial oxidation processes use bismuth molybdates and similar mixed oxides as selective catalysts. That oxygen species on the surface and in the bulk of lattices of these catalysts play important roles in such processes is established, even though the exact nature of this role is not fully known (see, for example, Ref. (*1*)). Several experimental investigations have considered different aspects of the problem. The early work of Keulks (*2*), Wragg *et al.* (*3*), and Sancier *et al.* (*4*) indicates that there is at least partial loss of lattice oxygen to the reactant species and that the contribution of lattice oxygen increases at higher temperatures. The behavior of the surface lattice oxygen species in the absence of a hydrocarbon reactant has been investigated experimentally by Ruckenstein *et al.* (*5*), and by Yong *et al.* (*6*) when the bismuth molybdate was reduced. Since such experiments of necessity couple the behavior of oxygen ions in various lattice positions, there is some difficulty in interpreting these quantitative results. In what follows calculations are performed to obtain the activation energies for bismuth-bound oxygen, molybdenum-bound oxygen, and the oxygen in the intermediate layer.

In the present work we use the method of minimum energy paths to describe the initial loss of lattice oxygen ion from the surface of the bismuth molybdate to outside but near the lattice. Thus we obtain a picture of the depletion process of oxygen from bismuth molybdates and other mixed oxides.

MINIMUM ENERGY PATHS

The method will not be discussed in great detail here because it has been described elsewhere (*7*, *8*). Briefly, the entity (ion or atom) whose path is to be followed is assumed to be mobile while other ions in and perhaps around the lattice are considered stationary. From the assumption of

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pairwise additivity, the interaction energy between the entity of interest (subscript j) and the fixed lattice is

$$E_j(l,m,n) = \sum_k E_{jk}(r_{jk}),$$

where the summation is over all ions of all species in all unit cells of the lattice. The position of j is described by coordinates (l,m,n). The individual interaction energy term E_{jk} depends upon the nature and species of j and k. This term can be obtained as a function of the separation distance r_{jk} from experimental data or can be estimated theoretically. A relatively simple method for the latter procedure has been brought together from various sources in Ref. (*7*).

The mobile ion will tend to be found where E_j is at least a local minimum. Consequently any two coordinates of j (say, l and m) can be obtained as a function of the third (n in this case) from

$$\frac{\partial E_j}{\partial l} = 0$$

$$\frac{\partial E_j}{\partial m} = 0.$$

Coordinates l and m describe the preferred path of j in the n direction. The corresponding value of E_j plotted as a function of the specified coordinate n is called the energy path of the mobile species.

The ions of interest in this work are lattice O^{2-} ions of different types on the surface of the bismuth molybdate. The types of O^{2-} ions are described in the following section. Figure 1 shows interaction energies calculated for individual ion pairs O^{2-}–O^{2-}, O^{2-}–Bi^{3+}, and O^{2-}–Mo^{6+} using the procedure of Ref. (*7*). This procedure does not consider some secondary aspects of ion pair potentials such as relativity effects (*9*) and non-pairwise additivity of electron clouds (*10*). However, it is shown below that the interaction energies are consistent with the structure of the experimental Bi_2MoO_6 unit cell. Hence Fig. 1 represents useable approximations in this case.

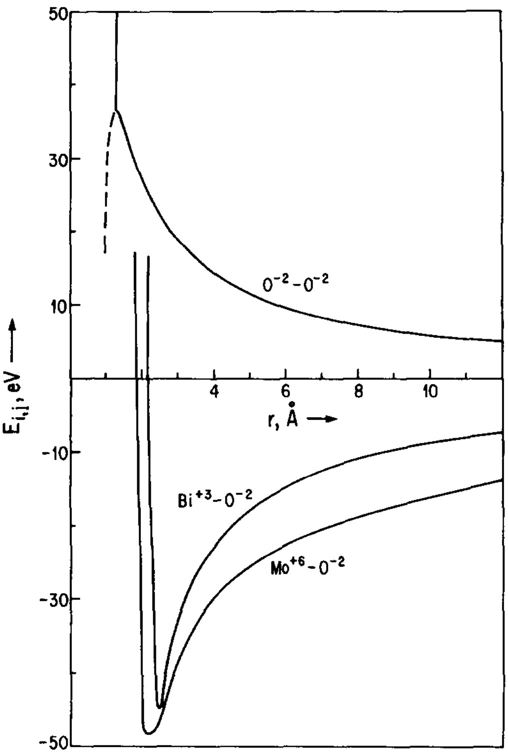

FIG. 1. Interaction potentials O^{2-}–O^{2-}, Mo^{6+}–O^{2-}, and Bi^{3+}–O^{2-}. The separation distance r is in Å, the potentials E in eV. For O^{2-}–O^{2-}, the potential is assumed to be infinite at distances less than the artificial maximum.

Preferred paths and energy paths of the different O^{2-} ions leaving the lattice under various conditions are calculated using the energies described in Fig. 1 and will be described in later sections.

BISMUTH MOLYBDATE LATTICE FOR THE ENERGY PATH

In this work, attention is restricted to the compound Bi_2MoO_6, the γ-phase. The lattice consists of a central unit cell surrounded symmetrically by other unit cells in the $\pm X$ and $\pm Z$ directions. The external surface of the lattice is considered to lie on the $Y = 0$ plane; consequently unit cells exist in the $+Y$ direction from the central unit cell but not in the $-Y$ direction. Since numerical computations require a finite lattice, the infinite lattice is truncated after unit cells that are one lattice parameter from the central cell in the $\pm X$, $+Y$, and $\pm Z$ directions. This "working lattice" is illustrated in Fig. 2. Of course the interaction energy of the mobile ion with the working lattice is different from that with the appropriately infinite lattice. However this difference is almost independent of the position of the ion, so the preferred path of the ion is only negligibly altered.

The surface O^{2-} ions will be considered to leave from the central unit cell, which is detailed in Fig. 3. Coordinates X, Y, and Z are nondimensionalized with respect to c_1, c_2, c_3, the dimensions of the unit cell in the three directions respectively, where $c_1 = c_2 = 5.5$ Å, $c_3 = 16.1$ Å. Oxygen ions 1 through 4 in the plane $Z = 0$, and 18 through 21 at $Z = 0.5$, lie in the Mo layer. Oxygen ions 5 through 9 ($Z = 0.12$) and 14 through 17 ($Z = 0.38$) lie in the so-called intermediate layer. Oxygen ions 10 through 13 lie in the Bi layer.

One of each of the different types of oxygen ions (Bi, intermediate, and Mo layer) at or near (inside) the external surface of the lattice at $Y = 0$ is now considered to leave the lattice. The corresponding energy paths under various conditions are presented in the next section.

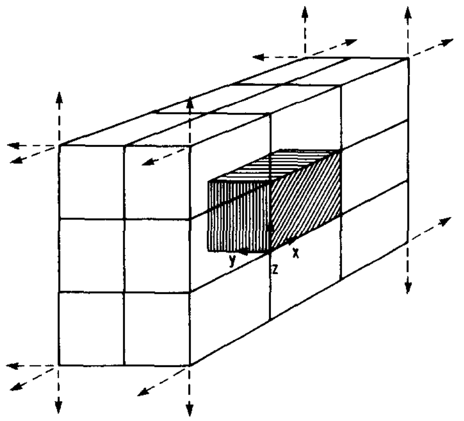

FIG. 2. Truncated lattice used in the computations of the total interaction energy for a mobile O^{2-} ion. The central unit cell, shown shaded, lies on the external surface of the total lattice at $Y = 0$. One unit cell is considered in each of the $\pm X$, $+Y$, and $\pm Z$ directions around the center unit cell. The dashed arrows show the directions in which the truncated lattice can be extended to form the full lattice.

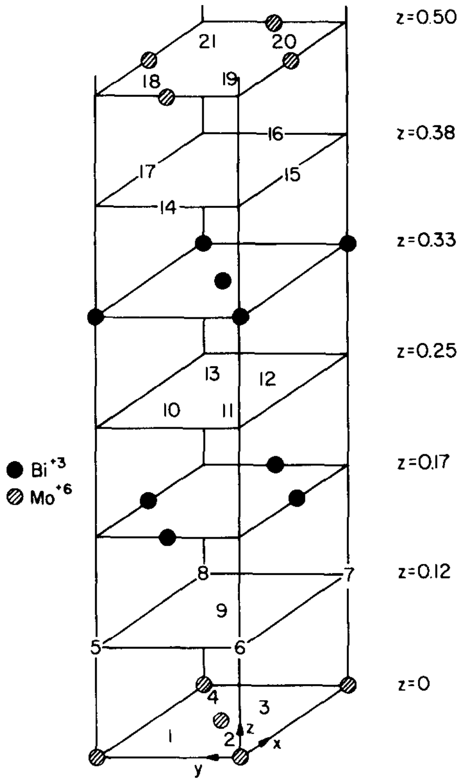

FIG. 3. Lower half of an idealized unit cell of 2 : 1 bismuth molybdate (Bi_2MoO_6). The upper half is a mirror image of this arrangement through $Z = 0.5$. The location of each Bi^{3+} ion is denoted by a filled circle and that of a Mo^{6+} ion by a shaded circle. Each O^{2-} ion is denoted by a serial number, 1 through 21, which identifies the ion in the text.

RESULTS

a. Energy Paths of Intermediate-Layer and Mo^{6+}-bound O^{2-} Ions Leaving the Filled Lattice

Note that the interionic interaction potentials of Fig. 1, following the procedure of Ref. (7), were obtained independently of the lattice parameters of Bi_2MoO_6. Consequently, the equilibrium position of the ion using the experimentally obtained lattice parameters, i.e., the position of the ion in Fig. 3, can be compared with that computed using the interaction parameters, i.e., the nearest computed local minimum. The difference between the two positions can be taken as a measure of consistency between the interaction potential parameters and the lattice parameters. Such a measure can be obtained from Figs. 4 and 5 which describe the energy paths of oxygen ions 15 (intermediate layer) and 19 (Mo-bound) respectively from the central unit cell out of the lattice in the $-Y$ direction. The motion of the ions in the figures is from left to right. The position of each ion according to the lattice parameters is given by the Y-coordinate at the start (left-most point) of each path, $Y = 0$ in Fig. 4, $Y = 0.25$ in Fig. 5. The Y-coordinate at the first (left-most) local minimum of energy represents the computed position of the ion as given by the interaction potentials. These positions correspond to $Y = -0.03$ in Fig. 4 and $Y = 0.24$ in Fig. 5. Note that the difference between the two positions is small, both in Fig. 4 and in Fig. 5. Consequently, the interaction potentials described in Fig. 1 can be used in the present case.

The difference in the values of E between the first (left-most) minimum and the maximum in Figs. 4 and 5 can be considered a measure of the ease with which the corresponding ion leaves the lattice. In the case of the ion in the intermediate layer, ion 15, ΔE is approximately 2 eV. For the Mo-bound ion, Fig. 5, the value is higher, approximately 3 eV.

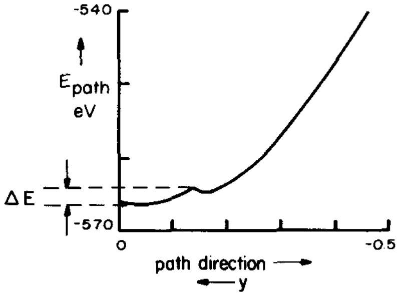

FIG. 4. Energy path of O^{2-} ion 15, in an intermediate layer of the central unit cell, leaving the Bi_2MoO_6 lattice through the $Y = 0$ surface. The initial position of the ion is the location of ion 15 in Fig. 3, corresponding to $Y = 0$. The motion of the ion is from left to right in the figure.

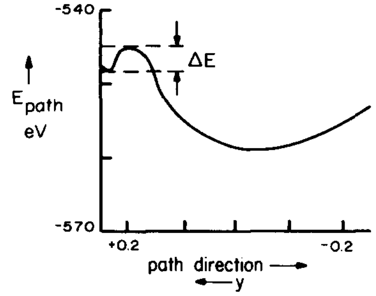

FIG. 5. Energy path of O^{2-} ion 19, bound to a Mo^{6+} ion in the center unit cell, leaving the Bi_2MoO_6 lattice through the $Y = 0$ surface. The initial position of the ion is as given in Fig. 3, corresponding to $Y = 0.25$. The motion of the ion is from left to right in the figure.

b. Energy Path of Bi^{3+}-Bound O^{2-} Ion Leaving the Filled Lattice

Now consider a bismuth-bound O^{2-} ion lying near the $Y = 0$ surface. Figure 6 illustrates the energy path of one such ion, number 11, leaving the surface. This energy path is qualitatively different from those of Figs. 4 and 5. Note the enormous energy barrier to be overcome before the ion can even approach the external surface of the lattice. Inspection of the preferred path at the bottom of Fig. 6 indicates that the energy barrier arises due to the interaction of the mobile ion with oxygen ion number 15 of Fig. 3.

DISCUSSION AND CONCLUSION

In terms of the ease of displacement, two types of oxygen ions can be distinguished in the filled ideal bismuth molybdate lattice. Oxygen ions bound to Mo^{6+} ions and those in the intermediate layer can be removed relatively easier than O^{2-} ions bound to Bi^{3+} when all cations and anions are present in the lattice, i.e., in the absence of vacancies.

Note that the energy barriers shown in Figs. 4 through 6 are those corresponding to O^{2-} ions moving out of (but near the surface of) the lattice. If a reaction occurs, oxygen can be considered to leave the lattice as O^{2-} ions. In the absence of the reaction, however, O^{2-} ions leaving the lattice would do so as neutral O_2 molecules.

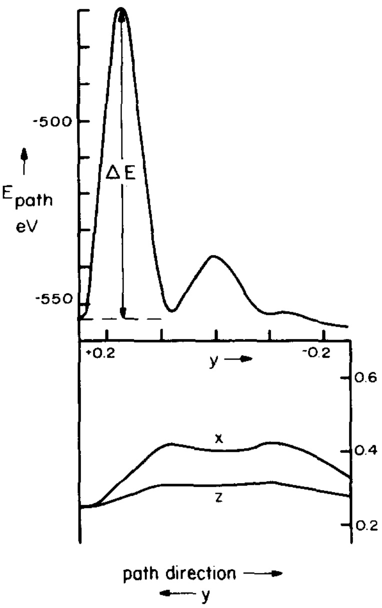

FIG. 6. Energy path of O^{2-} ion 11, bound in a Bi^{3+} ion in the central unit cell, leaving the Bi_2MoO_6 lattice through the $Y = 0$ surface (upper diagram). The preferred path of the ion, relating X and Z coordinates of the location of the ion to the Y coordinate, is given in the lower diagram. In both diagrams, the initial position of the ion is as given in Fig. 3, corresponding to $Y = 0.25$. The motion of the ion is from left to right in the figures.

However, even in this case, it is reasonable to suppose that the order of increasing energy barriers will not change, i.e., that the energy barrier for loss of an intermediate-layer O^{2-} ion as O_2 is less than that for a Mo^{6+}-bound O^{2-} ion as O_2, which is less than that for a Bi^{+3}-bound O^{2-} ion as O_2.

During selective oxidation, however, some indications (*7, 11, 12*) are that it is the O^{2-} ions in the bismuth layers of the lattice that are removed by the hydrocarbon molecules during their oxidation. If this is so, then the presence of the hydrocarbon can be expected to assist the process by decreasing the energy barrier required for transfer of the O^{2-} ion, compared with the value obtained here. This is probably not enough. Some significant changes in the unit cell, from its completely filled ideal state as indicated in Fig. 3, are needed for the removal of bismuth-bound O^{2-} ions to take place and for oxidation to proceed. One such plausible change is described below.

Recall that the energy barrier of Fig. 6 arises due to the interaction of the mobile O^{2-} ion with stationary O^{2-} ions either in the intermediate layer of the lattice or bound to Mo^{6+} ions. If some of these were to be removed, it is not inconceivable that the energy barrier to the removal of Bi-bound O^{2-} ions from the lattice could be significantly lowered. Removal of these O^{2-} ions could occur in several ways. First, O^{2-} ion vacancies are bound to exist in the "real" bismuth molybdate lattice. Additional vacancies can form during the oxidation itself, or may be produced prior to this by a prereduction process. Indeed, experiments (*6*) show that the number of anion vacancies in the bismuth molybdate lattice increases by an order of magnitude after prereduction. In fact such prereduced catalysts yield more reproducible results, when compared with unreduced catalysts. It is reasonable to suppose that exposing samples of bismuth molybdate containing different levels of anion vacancy to the same reducing conditions would result in the different samples now having equivalent amounts of anion vacancies. Consequently, bismuth-bound O^{2-} ions could now leave the different samples with equal ease, thus allowing reproducibility in catalytic performance.

The energy paths of the Bi^{3+}-bound O^{2-} ion in lattices containing O^{2-} ion vacancies are different from those given here and will be discussed in a later paper.

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