General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)
Mechanism for Sulfate Formation
by
S. P. Mehandru

and

Alfred B. Anderson

Chemistry Department, Case Western Reserve University

Cleveland, Ohio 44106

Abstract

Calculations based on the atom superposition and electron delocalization molecular orbital (ASED-MO) technique suggest that O₂ will adsorb preferentially end-on at an angle 45° from normal on a nickel cation site on the (100) surface of NiO. SO₂ adsorption is also stronger on the nickel site; SO₂ bonds through the sulfur atom in a plane perpendicular to the surface. Adsorption energetics for SO₃ on the nickel and oxygen sites are comparable in the preferred orientation in which the SO₃ plane is parallel to the surface. The calculations suggest that the strength of adsorption varies as O₂>SO₂>SO₃. On activation, SO₃ adsorbed to an O²⁻ site forms a trigonal pyramidal SO₄ species which yields, with a low barrier, a tetrahedral sulfate anion. Subsequently the anion reorients on the surface. Possibilities for alternative mechanisms which require the formation of Ni³⁺ or O¹⁻ are discussed. NiSO₄ thus formed leads to the corrosion of Ni at high temperatures in the SO₂+O₂/SO₃ atmospheres, as discussed in the experimental literature.

†On leave from KM College, Delhi University, Delhi 110007, India
Introduction

The corrosion of nickel and nickel-based alloys in SO$_2$ and SO$_2$+O$_2$/SO$_3$ atmospheres has been investigated by several workers in the past.\textsuperscript{1-9} Oxidation of nickel before it comes in contact with SO$_2$ gas results in the formation of an adherent protective scale of NiO on the nickel surface. This scale should, at first sight, prevent rapid corrosion of nickel in SO$_2$ atmospheres. Experimental results indicate that the corrosion rates of nickel in SO$_2$ atmospheres in the absence of O$_2$ at 600 °C are $10^4$ to $10^6$ times faster than its oxidation rate in 1 atmosphere oxygen.\textsuperscript{1} This enormous difference has been attributed to the rapid transport of nickel through a continuous Ni$_3$S$_2$ phase in the NiO scale. It has been observed that the NiO scale cracks after an incubation period of 1 to 24 hours (depending upon the temperature and SO$_2$ pressure) presumably because of stresses generated by sulfide formation at the scale-nickel interface by molecular transport of SO$_2$ through the physical defects in the NiO scale.\textsuperscript{2,3} This may be followed by the rapid inward diffusion of SO$_2$ through the cracks to the metal surface resulting in rapid corrosion.\textsuperscript{2} The corrosion behavior at 500-900 °C of preoxidized nickel in an SO$_2$+O$_2$/SO$_3$ environment, however, has been observed to be significantly different. Scale porosity is not a factor in the SO$_2$+O$_2$/SO$_3$ environment whereas it is definitely important in SO$_2$ atmospheres.\textsuperscript{3} This led previous workers to conclude that the initial reaction in the presence of SO$_3$ takes place on the NiO surface rather than at the nickel-nickel oxide interface. It is believed that nickel sulfate forms according to the reaction

$$\text{NiO(s)} + \text{SO}_3(g) \rightarrow \text{NiSO}_4(s)$$  \hspace{1cm} (1)
NiSO₄ is thermodynamically stable only when the effective pressure of SO₃ in the gas mixture is higher than its equilibrium pressure in reaction (1). Rapid corrosion rates of nickel are observed when it is surrounded by a Pt catalyst¹,³⁻⁵ which speeds the attainment of the SO₂ + ½O₂ ⇌ SO₃ equilibrium. This shows the importance of SO₃ in the preliminary step of the overall corrosion reaction. The fact that NiSO₄ has been difficult to detect on the surface led to the conclusion that it must react rapidly with nickel which is diffusing outward through the NiO scale to form the sulfide phase according to the reaction¹,⁴⁻⁷

\[
9\text{Ni}(s) + 2\text{NiSO}_4(s) \rightarrow \text{Ni}_3\text{S}_2(s) + 8\text{NiO}(s)
\] (2)

In fact, powdered mixtures of Ni and NiSO₄ have been found to react rapidly above 500 °C to form NiO and Ni₃S₂.⁴ The rate of sulfide formation is, therefore, highly likely to depend on the rates of the proposed reaction steps (1) and (2).

In order to explain the mechanism of formation of the sulfide phase, it was tentatively assumed in Ref. 4 that the tendency for adsorption on the surface varies as SO₃>SO₂>O₂. Our results in this paper, however, suggest that the order is just the reverse. Therefore, the purpose of this paper is two-fold: firstly, to calculate the relative adsorption energies of O₂, SO₂, and SO₃ molecules on the NiO surface and to understand the binding of these species from the molecular orbital point of view; and, secondly, to calculate the potential energy surface and thus devise a reaction path for reaction (1). We use the atom superposition and electron delocalization molecular orbital (ASED-MO) theory which has been previously used in studying a number of sulfate formation mechanisms.¹⁰
Method of Calculation

The ASED-MO theory\textsuperscript{11} is a semi-empirical technique based on an exact model in which the electronic charge density of a molecule or a solid is partitioned into a sum of rigid free atom components and a delocalization bond charge component. The superposition of rigid atom electron charge densities centered on the atomic nuclei yields, from the Hellmann-Feynman force theorem, a repulsive energy component, \( E_R \). The attractive bond charge related energy component, \( E_D \), is due to the interaction of a nucleus with the charge redistribution density according to the Hellmann-Feynman theorem. The sum is the exact molecular binding energy, \( E \):

\[
E = E_R + E_D
\]  

(3)

The \( E_D \) component of the total energy is not available but it has been found that the total molecular orbital energy, \( E_{MO} \), obtained from diagonalizing a one-electron hamiltonian which shares some features of the extended Hückel hamiltonian is often a satisfactory approximation to \( E_D \). We pay particular attention to ionization potentials\textsuperscript{12} and Slater orbital exponents\textsuperscript{13} used in the determination of \( E_{MO} \) to produce accurate charge transfers and bond lengths for diatomic species. The parameters so determined are the basis for studying structures and reactions of larger systems. The parameters used in this paper are given in Table I.

Nickel oxide has the rock-salt structure. We have employed a two layer thick cluster containing 42 ions (21 nickel cations and 21 oxygen anions). The first layer consists of 9 Ni\( ^{2+} \) and 12 O\( ^{2-} \) ions, with the central Ni\( ^{2+} \) ion surrounded by fully coordinated cations and anions in the same layer. This Ni\( ^{2+} \) ion was used for
all adsorption studies on the Ni$^{2+}$ site. The second layer has 12 Ni$^{2+}$ and 9 O$^{2-}$ ions, with central O$^{2-}$ ion surrounded by fully coordinated cations and anions in the same layer. This O$^{2-}$ ion was used for all adsorption studies involving the O$^{2-}$ site. The two layers of the Ni$_{21}$O$_{21}$ cluster are shown in Fig. 1. There are 42 unpaired electrons in the cluster because each d$^8$ Ni$^{2+}$ cation has two unpaired electrons. This is consistent with allocating at least one electron to all the d band levels. For all our calculations, the heights of adsorbate molecules are optimized to the nearest 0.05 Å, the bond lengths to the nearest 0.01 Å, and the bond angles to 5 deg. The calculated O$_2$ bond length is 1.38 Å, somewhat overestimating 1.22 Å from experiment. The S-O bond lengths in SO$_2$ and SO$_3$ are 1.45 Å and 1.43 Å, respectively, compared to 1.43 Å from experiment for both. The calculated SO$_2$ bond angle is 119 deg compared to 119.5 deg from experiment.

**Adsorption of O$_2$, SO$_2$, and SO$_3$ on NiO**

We have calculated the structures and adsorption energies of O$_2$, SO$_2$, and SO$_3$ molecules on our nickel oxide cluster model (Fig. 1). For O$_2$, both end-on (perpendicular and bent) and side-on (parallel) orientations on the central Ni$^{2+}$ and O$^{2-}$ ions of the cluster have been considered. The heights of O$_2$ above the surface site as well as the O-O bond length and tilt from the normal are completely optimized. Adsorption of SO$_2$ through the sulfur atom, as well as through the two oxygen atoms, is studied on the Ni$^{2+}$ and O$^{2-}$ sites. The SOO plane is kept perpendicular to the surface and the height, S-O bond lengths, and OSO angle are optimized. For SO$_3$ three orientations have been tried on the Ni$^{2+}$ and the O$^{2-}$ ions of
Fig. 1. A and B represent the two layers of the cluster model $\text{Ni}_{21}\text{O}_{21}$. For all adsorption studies on $\text{Ni}^{2+}$ site, layer A is on the top and layer B on the bottom. For all adsorption studies involving $\text{O}^{2-}$ site, layer B is on the top and layer A on the bottom.
the cluster. For the first orientation, binding is considered through the sulfur atom; the molecule is kept parallel to the surface and its height and the S-O bond lengths are optimized. In the second orientation SO\textsubscript{3} is constrained to bind to the surface Ni\textsuperscript{2+} and the O\textsuperscript{2-} ions through one of its oxygen atoms with the plane of the molecule perpendicular to the surface and then the height and the S-O bond lengths are completely optimized. In another orientation on O\textsuperscript{2-}, SO\textsubscript{3} is allowed to bind to the surface through its two oxygen atoms. All these orientations for O\textsubscript{2}, SO\textsubscript{2}, and SO\textsubscript{3} are illustrated in Fig. 2.

The calculated results for O\textsubscript{2} adsorption on the Ni\textsubscript{21}O\textsubscript{21} cluster model are given in Table II. At first, perpendicular and parallel O\textsubscript{2} orientations are tried on the surface anion and cation sites. Of these, perpendicular coordination to Ni\textsuperscript{2+} is most favored. In this case the O\textsubscript{2} bond is found to stretch slightly by 0.06 Å. Subsequent tilting produces additional stability, which is maximum at 45 deg from the surface normal. At this angle the O\textsubscript{2} bond stretches too much according to our non-self-consistent method, dissociating to produce oxide anions because the O 2p energy levels lie below the Ni valence band. In fact a charge self-consistent method would prevent this, but our result indicates that there is further weakening of the O\textsubscript{2} bond associated with the bending. When O\textsubscript{2} is coordinated parallel to a Ni\textsuperscript{2+} site, its bond shrinks by 0.05 Å. Perpendicular and parallel O\textsubscript{2} orientations at the anion site produce less stability than the cation site. Tilting O\textsubscript{2} in the perpendicular orientation results in a slow and then rapid stabilization as it transfers to a neighboring Ni\textsuperscript{2+} site. The nature of the coordination bond between O\textsubscript{2} and Ni\textsuperscript{2+} may
Fig. 2 Orientations of $O_2$, $SO_2$, and $SO_3$ studied on the Ni$^{2+}$ and O$^{2-}$ ions of the Ni$_{21}$O$_{21}$ cluster model. Only that surface ion is shown on which the adsorption is considered. Lengths are Å and angles are deg.
be understood from the energy level correlation diagram in Fig. 3.
The first column of energy levels shows the valence levels of O₂;
the second column shows how they shift as a result of the 0.06 Å
stretch; and the third shows the results of interacting with the
cluster, for which levels are given in the fourth column. It may
be seen that there is an important O₂ ωp donation bond to the Ni²⁺
d₂ orbital and that its antibonding counterpart lies high and,
assuming the cluster spin does not change, it is empty. The O₂
orbitals form bonding and antibonding counterpart orbitals with
what is formally labeled the O 2p band. There is no net bond order
due to these interactions. It must be remembered that the O 2p
band consists in Ni²⁺ + O 2p bonding orbitals which are predomi-
nantly O 2p in character but have some Ni d contributions. This
is why the O₂ π orbitals interact with the O 2p band when co-
ordinated to Ni²⁺. The O₂ π* orbitals form bonding orbitals with
the Ni 3d band and they are doubly occupied. The antibonding
counterpart orbital energy levels lie in the half-filled region, so
there is a net back-donation to the O₂ π* orbitals which con-
tributes to the adsorption bond order. The cause of the bending of
O₂ away from the surface normal is evident in Fig. 3. With
bending, the strength of the overlap between the πₜ orbital and the
dₓz orbital of Ni²⁺ decreases, resulting in reduced antibonding
and, therefore, stability. As may be seen, two levels have dropped
below the πᵧ, dyz antibonding orbital levels; prior to bending they
were degenerate. The resultant effect of all donation and back-
donation interactions is a Mulliken charge transfer of 0.5 electron
to the O₂ molecule, which weakens it and causes it to stretch. In
Fig. 3. Molecular orbital correlation diagram for O$_2$ adsorbed on the Ni$^{2+}$ site in the end-on and bent orientation. The second column shows the energy levels of adsorbed O$_2$ without the surface. Correlation lines are drawn for orbitals which have 0.05 or more electronic charge on O$_2$. 
the parallel orientation the charge transfer is less, 0.1, and the
O₂ bond shrinkage is probably a consequence of increased 2-6
bonding overlap and covalent stabilization.

The calculated structure and adsorption energy of SO₂ adsorbed
through the sulfur atom on the Ni²⁺ and the O²⁻ sites of the
cluster are tabulated in Table III. On adsorption the S-O bonds
are shortened by 0.06 Å and the OSO angle increases by 10 deg on
the Ni²⁺ site and 20 deg on the O²⁻ site, compared with the corre-
spounding gas phase values. Adsorption is stronger on the Ni²⁺ site,
as was the case for O₂. The orbital correlation diagram for SO₂
adsorbed on the Ni²⁺ ion is shown in Fig. 4. The second column
shows the energy levels of SO₂ having the structure of the adsorbed
molecule but with the surface removed. The lowest 2z₁ orbital of
SO₂ is stabilized by a negative overlap, a phenomenon which has
been seen in a variety of other studies as well,¹⁰c,₁₄-₁₆ and has
been explained by Whangbo and Hoffmann using perturbation theory.¹⁵
This interaction yields a net stabilization because the antibonding
counterpart lies high in the Ni 4p band, which is empty. The other
significant interaction of SO₂ with NiO involves its 5a₁ orbital,
the highest occupied orbital, with the d₂2 orbital of Ni²⁺ ion, the
antibonding combination of which is half-filled. This results in
charge transfer from SO₂ to the Ni 3d band. There is however a
weak back-donation to the 2b₁ orbital of SO₂, the lowest unoccupied
orbital, to the dᵧz orbital of Ni²⁺ ion. The net result is a
transfer of about 0.3 electron from SO₂ to the nickel oxide. It is
the reduction in occupation of the 5a₁ orbital which causes the OSO
angle to increase by 10 deg, an expected result of molecular
orbital theory.¹⁷ For this reason an increase in the OSO angle is
Fig. 4. Same as in Fig. 3 for SO$_2$ adsorbed through sulfur on the Ni$^{2+}$ site with its plane perpendicular to the surface. The second column shows the energy levels of adsorbed SO$_2$ with the surface removed. Correlation lines are drawn for orbitals which have 0.2 or more electron on SO$_2$. 
also predicted for \( \text{SO}_2-\text{O}^{2-} \) coordination and even for a mode of coordination where two oxygen atoms of \( \text{SO}_2 \) bond to two \( \text{Ni}^{2+} \) while bridging a central \( \text{O}^{2-} \) (Table III). Interestingly, in this last case, the \( 5a_1 \) donation to the \( \text{Ni}^{2+} \) ions is through \( p_z \) orbitals on the oxygen atoms.

Table IV contains the calculated results for \( \text{SO}_3 \) adsorbed on the \( \text{Ni}^{2+} \) and the \( \text{O}^{2-} \) ions in all of the orientations described previously. As may be seen from this Table, adsorption energies for the parallel orientations far exceed those for the perpendicular orientations. Adsorption energies of \( \text{SO}_3 \) in the parallel orientation on the \( \text{Ni}^{2+} \) ion and the \( \text{O}^{2-} \) ion are within 0.2 eV of each other with \( \text{Ni}^{2+} \) site slightly favored. The S-C bonds are shortened by 0.02 Å and they bend upward by 5 deg when adsorbed on the \( \text{Ni}^{2+} \) site. The bending is caused in part by the small (0.01) negative Mulliken overlap between the oxygen atoms of \( \text{SO}_3 \) and the \( \text{O}^{2-} \) anions in the surface. The molecular orbital correlation diagram for \( \text{SO}_3 \) adsorbed on the \( \text{Ni}^{2+} \) site in the parallel orientation is shown in Fig. 5. The lowest orbital, \( 2a_1' \), of \( \text{SO}_3 \) is stabilized by a negative overlap as discussed earlier for \( \text{SO}_2 \). This interaction accounts almost entirely for the adsorption stabilization. The lowest empty orbital, \( 2a_2' \), of \( \text{SO}_3 \) is stabilized by in-phase interaction with \( d_z^2 \) of \( \text{Ni}^{2+} \) and this gives rise to charge transfer (−0.4) from the \( \text{Ni} 3d \) band to \( \text{SO}_3 \). The corresponding antibonding counterparts lie high above and are empty. This orbital, being partially occupied, also contributes to the bending according to standard ideas of molecular orbital theory.17
Fig. 5. Same as in Fig. 3 for SO$_3$ adsorbed in parallel orientation on the Ni$^{2+}$ site. Correlation lines are drawn for orbitals with 0.2 or more electron on SO$_3$. 
Mechanism of Sulfate Formation on Nickel Oxide in the Presence of O₂, SO₂, and SO₃

If we compare the calculated adsorption energies of O₂, SO₂, and SO₃ on the Ni²⁺ and the O²⁻ sites of the Ni₂₁O₂₁ cluster model, given in the previous section, the adsorption is favored on the nickel site for all the species. Thus if adsorption studies of each of these species on NiO are made at low temperatures and ultra high vacuum conditions, then they will adsorb on the Ni²⁺ ions of the oxide. However, if they are present at the same time at low temperatures and pressures, adsorption of O₂ on Ni²⁺ sites is preferred, thus blocking the nickel cations so that adsorption of SO₂ and SO₃ will be prevented. At high temperatures and pressures desorption will compete with adsorption and there is a likelihood of all species getting adsorbed and desorbed establishing a dynamical equilibrium between the condensed phase and the gaseous phase. Occasionally some SO₃ molecules will get adsorbed on the O²⁻ sites of the oxide surface forming a trigonal pyramidal SO₄ structure. We have calculated the reaction pathway for this trigonal pyramidal SO₄ species to convert to tetrahedral SO₄. We calculate no activation barrier for the surface oxygen anion to come out of the surface plane accompanied by an umbrella distortion of S-O bonds, along with reorientation of SO₄ species until bonds are established between the two neighboring nickel cations and the lower two oxygens of SO₄. The calculated structure of the coordinated sulfate is shown in Fig. 6. The calculated reaction energy of SO₃ and the Ni₂₁O₂₁ cluster model to give coordinated sulfate is 2.53 eV, about 1.1 eV more stable than the planar SO₃ adsorbed on the O²⁻ site of the cluster. The energetics for SO₄ formation from
Fig. 6. Reaction pathway when adsorbed SO$_3$ on O$_{2^-}$ ion is converted to coordinated sulfate.
SO$_3$ and Ni$_{21}$O$_{21}$ cluster are also shown in Fig. 6. Our calculated reaction energy compares favorably with 2.61 eV calculated from the heats of formation values for the reactants and products of the reaction (1).\textsuperscript{18} Although our calculations produce no barrier for sulfate formation from SO$_3$ and Ni$_{21}$O$_{21}$, in practice, however, there may be a small barrier for displacing the O$_2$ molecules on the Ni$^{2+}$ sites by SO$_3$ on the O$^{2-}$ sites.

The orbital correlation diagram for SO$_4$ coordinated to Ni$_{21}$O$_{20}$ cluster is shown in Fig. 7. The lowest a-symmetry sulfate orbital is stabilized by negative overlap with the Ni P$_2$-orbitals. There are at least three other sulfate orbitals which show prominent in-phase stabilizations with t.e. Ni s orbitals but their antibonding counterparts are also doubly occupied which makes these interactions closed-shell and non-bonding. However, the upper three filled orbitals of SO$_4$ are stabilized by mixing with Ni d orbitals and their antibonding combinations lie in the half-filled region of the Ni 3d band. This gives rise to charge transfer from SO$_4^{2-}$ to the Ni 3d band. Our calculations produce a net charge of -0.3 on the coordinated SC$_3$ species.

At high O$_2$ pressures, alternate pathways to sulfate formation can be considered. It is commonly believed\textsuperscript{19} that Ni$^{3+}$ and O$^{1-}$ form on the surface of NiO at high O$_2$ pressures. Therefore, under such conditions SO$_3$ may be expected to adsorb to O$^{1-}$ centers as well as O$^{2-}$ centers, leading to the formation of sulfate. In the former case, as the sulfate anion forms, additional Ni$^{3+}$ is created. Since Ni$^{3+}$ is uncommon in solid nickel compounds it is relatively unstable and so may retard sulfate formation by SO$_3$
Fig. 7. Orbital correlation diagram showing $\text{SO}_4^{2-}$ coordination to $\text{Ni}_{21}\text{O}_{20}^{2+}$ cluster. Correlation lines are drawn for orbitals with 0.2 or more electron on $\text{SO}_4$. 
attack on $O^{1-}$, should $O^{1-}$ form on the surface. Another pathway might have $SO_3$ attack the upright activated adsorbed $O_2$, just as in our past study of sulfate formation on a NaCl surface.\textsuperscript{10b} This reaction would lead to the formation of $3 \, Ni^{2+}$ or $3 \, O^{1-}$ whose relative instability may retard this pathway to sulfate formation. On the NaCl surface $Cl^{1-}$ is oxidized to $Cl_2$, a facile reaction. In the case of sulfate formation from $SO_2$ and a bis(phosphine) Pt dioxygen complex which we also studied theoretically,\textsuperscript{20} the platinum is oxidized to $Pt^{2+}$, a facile reaction. The techniques of surface science (HREELS, UPS, XPS, and Auger) are appropriate for evaluating the importance of the above alternative mechanisms on NiO. We encourage that such studies of $Ni^{3+}$, $O^{1-}$ and $O_2$ at the surface of NiO in the presence of $O_2$ be made.

Conclusions

Our study has characterized the binding of $O_2$, $SO_2$ and $SO_3$ to the (100) surface of NiO. $O_2$ is predicted to bond the most strongly of the three molecules and $SO_3$ the least strongly. All bind more strongly to the $Ni^{2+}$ cations than to the $O^{2-}$ anions. The order of adsorption energies is probably not critical to the sulfate formation reaction, which involves $O^{2-}$ donation to $SO_3$ to yield the $SO_4$ anion, because of the high gas pressures and temperatures of hot corrosion processes. According to our calculations, whenever $SO_3$ coordinates to a surface $O^{2-}$, sulfate is very likely to form because the calculated activation energy is low. We have not modeled the second step of the hot corrosion process, the reaction of nickel with the sulfate anion, in this study. However, it is known to proceed rapidly at high temperatures, just as does the
sulfate formation step. Finally, we encourage the surface science community to study the nickel oxide surface in the presence of O$_2$.

Acknowledgment

We thank the NASA Lewis Research Center for supporting this work through NASA Grant NAG-3-341.
References


18. Heats of formation for NiO(s), SO₃(g), and NiSO₄(s) are -58.4, -94.45, and -213.0 kcal/mole respectively. These values are taken from the Handbook of Chemistry and Physics, 43rd edition, C. D. Hodgman, Ed., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1962.
Table 1. Atomic parameters used in the calculations: Principal quantum number (n), ionization potential (IP) in eV, Slater exponents (\(\zeta\)), and respective coefficients (c) for double-\(\zeta\) d functions.

<table>
<thead>
<tr>
<th>Atom</th>
<th>s</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>IP</td>
<td>(\zeta)</td>
</tr>
<tr>
<td>Ni^{a}</td>
<td>4</td>
<td>9.635</td>
<td>1.800</td>
</tr>
<tr>
<td>S^{b}</td>
<td>3</td>
<td>22.200</td>
<td>2.220</td>
</tr>
<tr>
<td>O^{a,c}</td>
<td>2</td>
<td>27.480</td>
<td>2.046</td>
</tr>
</tbody>
</table>

^{a}Ref. 10a.

^{b}Ref. 19.

^{c}For the treatment of \(O_2\), 3d orbitals with ionization potential 2 eV and Slater exponent 2.00, are also used (Ref. 10b).
Table II. Calculated results for the height (h), the change in O-O bond length after adsorption, Δ(0-O), and the adsorption energy (ΔE) of O₂ on the Ni₂₁O₂₁ cluster model.

<table>
<thead>
<tr>
<th>Site</th>
<th>Orientationᵃ</th>
<th>h(Å)</th>
<th>Δ(0-O)(Å)</th>
<th>ΔE(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>End-on, 45 deg tilt</td>
<td>1.65</td>
<td>0.06</td>
<td>3.62</td>
</tr>
<tr>
<td></td>
<td>Parallel</td>
<td>2.25</td>
<td>-0.05</td>
<td>2.71</td>
</tr>
<tr>
<td>O</td>
<td>Perpendicular</td>
<td>2.95</td>
<td>0.00</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>Parallel</td>
<td>2.50</td>
<td>-0.01</td>
<td>2.39</td>
</tr>
</tbody>
</table>

ᵃSee Fig. 2.
Table III. Calculated results for the height (h) of the sulfur atom above the adsorption site, the change in S-O bond length, $\Delta(S-O)$, on adsorption, the OSO bond angle, and the adsorption energy ($\Delta E$) of SO$_2$ adsorbed on the Ni$_{21}$O$_{21}$ cluster model.

<table>
<thead>
<tr>
<th>Site</th>
<th>Orientation$^a$</th>
<th>h(A)</th>
<th>$\Delta(S-O)$(A)</th>
<th>$\angle$OSO(Deg)</th>
<th>$\Delta E$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Perpendicular through sulfur</td>
<td>2.05</td>
<td>-0.06</td>
<td>130</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>Perpendicular through oxygen</td>
<td>2.70</td>
<td>-0.06</td>
<td>140</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>Perpendicular through oxygen</td>
<td>2.62</td>
<td>-0.07</td>
<td>140</td>
<td>1.79</td>
</tr>
</tbody>
</table>

$^a$See Fig. 2.
Table IV. Calculated results for the height \( (h) \) of the sulfur atom above the surface site, the S-O bond length \( (R_{SO}) \), and the adsorption energy \( (\Delta E) \) of \( SO_3 \) when adsorbed on the \( Ni_{21}O_{21} \) cluster model.

<table>
<thead>
<tr>
<th>Site</th>
<th>Orientation(^a)</th>
<th>( h(\text{A}) )</th>
<th>( R_{SO}(\text{A}) )</th>
<th>( \Delta E(\text{eV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Parallel through sulfur</td>
<td>2.30</td>
<td>1.41</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>Perpendicular through one oxygen</td>
<td>3.25</td>
<td>(1.40, 1.42)(^b)</td>
<td>0.62</td>
</tr>
<tr>
<td>O</td>
<td>Parallel through sulphur</td>
<td>2.20</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>Perpendicular through one oxygen</td>
<td>4.32</td>
<td>(1.42, 1.43)(^b)</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Perpendicular through two oxygens</td>
<td>2.80</td>
<td>(1.41, 1.44)(^c)</td>
<td>0.68</td>
</tr>
</tbody>
</table>

\(^a\)See Fig. 2

\(^b\)The first number represents the bond length for one S-O bond perpendicular to the surface and the second number is the bond length for the other two S-O bonds of adsorbed \( SO_3 \).

\(^c\)The first number represents the bond lengths of the two S-O bonds through which \( SO_3 \) is binding to the surface and the second number is the bond length of the third S-O bond which is perpendicular to the surface.
Figure Captions

Fig. 1. A and B represent the two layers of the cluster model Ni_{21}O_{21}. For all adsorption studies on Ni^{2+} site, layer A is on the top and layer B on the bottom. For all adsorption studies involving O^{2-} site, layer B is on the top and layer A on the bottom.

Fig. 2. Orientations of O_2, SO_2, and S_2O_3 studied on the Ni^{2+} and O^{2-} ions of the Ni_{21}O_{21} cluster model. Only that surface ion is shown on which the adsorption is considered. Lengths are Å and angles are deg.

Fig. 3. Molecular orbital correlation diagram for O_2 adsorbed on the Ni^{2+} site in the end-on and bent orientation. The second column shows the energy levels of adsorbed O_2 without the surface. Correlation lines are drawn for orbitals which have 0.05 or more electronic charge on O_2.

Fig. 4. Same as in Fig. 3 for SO_2 adsorbed through sulfur on the Ni^{2+} site with its plane perpendicular to the surface. The second column shows the energy levels of adsorbed SO_2 with the surface removed. Correlation lines are drawn for orbitals which have 0.2 or more electron on SO_2.

Fig. 5. Same as in Fig. 3 for S_2O_3 adsorbed in parallel orientation on the Ni^{2+} site. Correlation lines are drawn for orbitals with 0.2 or more electron on S_2O_3.
Fig. 6. Reaction pathway when adsorbed SO$_3$ on O$^2-$ ion is converted to coordinated sulfate.

Fig. 7. Orbital correlation diagram showing SO$_4^{2-}$ coordination to Ni$_{21}$O$_{20}^{2+}$ cluster. Correlation lines are drawn for orbitals with 0.2 or more electron on SO$_4$. 