Dinitrosyl formation as an intermediate stage of the reduction of NO in the presence of MoO₃

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We present first-principles calculations in the framework of density-functional theory and the pseudopotential approach, aiming to model the intermediate stages of the reduction of NO in the presence of MoO₃(010). In particular, we study the formation of dinitrosyl, which proves to be an important intermediate stage in the catalytic reduction. We find that the replacement of an oxygen of MoO₃ by NO is energetically favorable, and that the system lowers further its energy by the formation of (NO)₂. Moreover, the geometry and charge distribution for the adsorbed dinitrosyl indicates a metal-oxide mediated coupling between the two nitrogen and the two oxygen atoms. We discuss the mechanisms for the dinitrosyl formation and the role of the oxide in the reaction.


I. INTRODUCTION

Reduction of nitric oxide (NO) has long been the focus of detailed studies, because of the role of NO as pollutant in the atmosphere. Three-way catalysts, based on Rh, Pt or PdO are used in automobile exhausts for this purpose; the effectiveness of such catalysts was found to increase when molybdenum oxides are added. Recently, it was proposed that the NO reduction products N₂ and O₂ are formed nondissociatively from NO via an adsorbed dinitrosyl species, which facilitates N–N coupling, since low temperature NO coupling remains unknown. To address this important question, we perform first-principles calculations based on density-functional theory and the pseudopotential approach, for various configurations involving nitrosyls and the MoO₃(010) surface. The paper is organized as follows: First, we review the structure of MoO₃ and describe the method we use for the calculations. Next, we present our results for the MoO₃(010) surface with an O vacancy, a structure with an exposed Mo atom which can adsorb NO molecules. This is followed by detailed analysis of the configurations involving adsorbed NO and (NO)₂. Finally, we discuss the dinitrosyl formation mechanisms and the role of the MoO₃(010) surface as a catalyst for the reduction of NO.

II. MOLYBDENUM TRIOXIDE

Molybdenum trioxide is a layered material, its layers being weakly bonded via van der Waals interactions. The space group is Q₁₆ (bnn), and the lattice is orthorhombic with parameters 3.962, 13.858, and 3.697 Å. Each unit cell contains four MoO₃ units. The lattice coordinates of the atoms are ±(x,y,z) and ±(±x, ±y, ±z), with (x, y) equal to (0.086, 0.099) for the Mo atoms, and (0.086, 0.250), (0.586, 0.099), (0.586, 0.431) for the three O atoms surrounding each Mo atom, respectively.

The MoO₃ crystal is shown in Fig. 1. Macroscopically, the material forms “small, thin, lustrous plates, parallel to (010).” This is revealed in the atomistic structure: It consists of bilayers parallel to the (010) plane, which are bonded through weak electrostatic interactions, with the (010) surface being the easy cleavage plane of the crystal. Each bilayer consists of two sublayers of periodically arranged distorted MoO₆ octahedra. There are three structurally different O atoms. The asymmetric bridging oxygen is collinear with two Mo atoms and forms one long and one short bond with them. The symmetric bridging oxygen is located between the two sublayers of the bilayer and bonds to two Mo atoms of one sublayer with equal bond lengths and to one Mo atom of the other sublayer with an elongated bond. Finally, the univalent terminal oxygen is connected to one Mo atom forming the shortest Mo–O bond in the system. The Mo–O bond lengths in MoO₃ as obtained from several experimental and theoretical studies are shown in Table I.

III. THE CALCULATION

All calculations reported in this work were performed via the High-performance-Fortran Adaptive Real-space Electronic Structure (HARES) package. We use density-functional theory (DFT) in the local spin density approximation (LSDA). The Kohn–Sham valence electron wave functions are represented in a real-space orthogonal grid with a spacing of 0.13 Å, which is equivalent to a cutoff energy of 150 Ry in a plane-wave basis calculation. The ionic cores and their interaction with valence electrons were taken into account by the pseudopotential method.
The reduction of NO in the presence of MoO₃

An O vacancy in MoO₃ is formed when a terminal oxygen atom is missing. As discussed in Sec. II, the terminal O is univalent and forms the shortest Mo–O bond in the bulk; this bond is also the strongest, with a calculated bond order of 1.93. Accordingly, it is expected that the formation energy of the vacancy will be high. Indeed, our calculation yields a formation energy of 2.95 eV/vacancy, assuming that the O atoms that leave the surface form O₂ molecules (see Table III). The (2 × 2) unit cell corresponds to a 0.25 ML coverage of vacancies, which is low enough to ensure that the interactions between vacancies are negligible. The formation of the O vacancy is accompanied by small relaxations of atoms around the missing terminal O atom. The relaxed geometry is shown in Fig. 2(a). The main effect is an inward displacement of the exposed Mo atom, which results in shrinking the Mo-symmetric oxygen bonds from 1.96 to 1.91 Å for O in the same sublayer and from 2.33 to 2.11 Å for O in the adjacent sublayer. None of the atoms has any significant displacement parallel to the (010) plane; we thus find no evidence of surface reconstruction due to vacancy formation.

The MoO₃(010) surface with a terminal oxygen vacancy, shown in Fig. 2(a), has many characteristics of a good catalytic platform: The exposed Mo atom promises to be chemically active and has the ability to bond to more than one adsorbate atom, since it has lost a double bond. The remaining terminal O atoms around the vacancy site form a cage structure that can enhance coupling between the adsorbates. In ideal MoO₃, the calculated population for a terminal O is −0.4 electrons, so the remaining terminal O at-

TABLE I. Bond lengths (in Å) between Mo and O in MoO₃ as calculated in the present work compared to other calculations (a) by Chen et al. (Ref. 15) and (b) by Yin et al. (Ref. 14) and to experimental data obtained from (c) the atomic positions given by Wyckoff (Ref. 6), (d) the work of Kihlborg (Ref. 21) as given in Ref. 15. The symbols O₉, O₁₀, and Oₑ₀ denote the terminal, symmetric bridging, and asymmetric bridging O atoms, respectively.

<table>
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<th>Bond</th>
<th>This work</th>
<th>Theory (a)</th>
<th>Theory (b)</th>
<th>Expt. (c)</th>
<th>Expt. (d)</th>
<th>Expt. (avg)</th>
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<td>2.08</td>
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</table>

FIG. 1. Structure of bulk MoO₃. Mo atoms are shown as larger gray spheres, O atoms as white, smaller spheres. The three different types of O atoms (terminal, asymmetric bridging, symmetric bridging) are indicated.
oms are expected to repel the adsorbates, creating an implicit attraction between them.

The first step in the catalytic reduction of NO is the adsorption of a NO molecule. The binding configuration is shown in Fig. 2(b). NO is bonded to a Mo atom and substitutes a terminal O. The molecule is perpendicular to the surface in the lowest energy geometry, rendering the dissociation of nitrosyl on the surface implausible. The adsorption of NO on MoO$_3$ with an O vacancy restores the positions of the surrounding atoms to their positions in the ideal MoO$_3$(010) surface: the lengths of the Mo–N and N–O bonds are 1.91 and 1.14 Å, respectively. The N–O bond has very similar length to the bond of a free NO molecule. We find this bond to be 1.15 Å, in excellent agreement to experiment.

The binding energy for NO to the MoO$_3$(010) surface with an oxygen vacancy is 2.98 eV/molecule. The energy difference between the MoO$_3$(010) surface and the same surface with NO substituting a terminal O is -0.03 eV/molecule, assuming that the O atoms leaving the surface form O$_2$ molecules. The system lowers its total energy by the substitution of terminal O by NO, so this configuration must be an important step in the NO reduction. The mechanism of the substitution and the formation of O$_2$ gas is not known, but it seems unlikely that the system passes through the O vacancy configuration, since the barrier for this path would be at least 2.95 eV, a number which would forbid the process under ordinary conditions. The transition state for the substitution could involve intermediate formation of NO$_2$ and/or O$_3$.

NO adsorption could also take place after a vacancy on the surface has been formed by an independent mechanism, for example, after a CO molecule has hit the surface and CO$_2$ has been formed. Another similar mechanism would be the formation of H$_2$O from gas-phase H$_2$ and a terminal O atom. The exact final product of the reduction of MoO$_3$(010) to MoO$_3(v)$(010) cannot be ad hoc determined, as it depends on the experimental conditions. However, the final state of the O atom that leaves the surface to create the vacancy would not affect the picture, as the energetics would not change dramatically. We therefore choose to use O$_2$ as a typical product of a reduction reaction.

V. DINITROSYL CHEMisorption

To study the energetics of the dinitrosyl adsorption, we consider two characteristic configurations: In the first, the (NO)$_2$ plane is parallel to (001) or the plane defined by the Mo atom and the symmetric bridging O atoms. In the second configuration, the (NO)$_2$ plane is parallel to (100), or a plane perpendicular to the previous one which contains the Mo atom and the asymmetric bridging O atoms. The relaxed geometries for both configurations are shown in Fig. 3.

In the first case, a reflection symmetry with respect to the (100) plane was imposed, following the experimental re-
results obtained on oxidized Mo(110).

Removal of the reflection symmetry does not result in further relaxation or significant lowering of the total energy, indicating that in the lowest energy geometry the two NO molecules of the dinitrosyl are identical. By contrast, (NO)$_2$ adsorbed parallel to the Mo-asymmetric O plane is found to be strongly asymmetric, with one of the two NO molecules closer to the Mo center than the other. This is a direct consequence of the asymmetry of the underlying oxygen atoms.

The bond lengths for both configurations, together with the bond lengths of the previously discussed structures are summarized in Table II. For adsorbed dinitrosyl in the Mo-symmetric O plane, the Mo–N bond is 2.00 Å long, 5% longer than in that of a single adsorbed NO. The Mo–N bond is weaker for adsorbed (NO)$_2$ as the bonding electrons of Mo are shared by two N atoms. The N–O bond length is 1.14 Å, identical to that of adsorbed NO. In the second configuration, having dinitrosyl in the Mo-asymmetric O plane, the Mo–N (N–O) bonds have lengths 1.95(1.15) and 2.35(1.13) Å, for NO above the long (2.18 Å) and short (1.90 Å) Mo-asymmetric O bond, respectively. Both N and O of the adsorbed nitrosyls are more strongly bound above the less strongly bonded asymmetric O.

The asymmetric configuration, with (NO)$_2$ parallel to the Mo-asymmetric O plane, has a slightly lower energy than the other, by 0.10 eV per (NO)$_2$ molecule. The binding energy to MoO$_3$(010) with an oxygen vacancy is 3.80 and 3.90 eV per molecule for the symmetric and asymmetric configuration, respectively. The energy gain when (NO)$_2$ substitutes a terminal O of MoO$_3$(010) with formation of O$_2$ gas is 0.85 and 0.95 eV per molecule for the two configurations.

The large lowering of the total energy by 0.90 eV on average per molecule for (NO)$_2$ adsorption, compared to 0.03 eV per NO for the NO adsorption, indicates that bonding between the two parts of the dinitrosyl has taken place. This bonding is evident in Fig. 4, which presents a contour plot of the total electronic density minus a superposition of atomic electronic densities on the dinitrosyl plane, which coincides with the symmetric bridging O plane. According to our choice of shading, electronic charge has moved from the darker to the lighter regions, relative to the charge distribution of a superposition of atomic densities. The white T-shaped clouds inside the slab correspond to symmetric bridging O atoms, while those at the bottom to terminal O atoms. Small gray spots in the middle of black regions correspond to Mo atoms. The two bright vertical complexes correspond to the two NO molecules. As the electronegativities of the involved elements dictate, charge has moved from the Mo atoms to N and O atoms, with O atoms having

<table>
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<th>Structure</th>
<th>Mo–O$_s$</th>
<th>Mo–O$_t$</th>
<th>Mo–O$_a$</th>
<th>Mo–N</th>
<th>N–O</th>
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FIG. 4. Contour plot of total electronic density minus a superposition of valence atomic charge densities in the Mo–N–O plane for adsorbed (NO)$_2$ parallel to the symmetric O plane. The background shade corresponds to zero; darker shades correspond to negative values, lighter shades to positive values.
slightly more charge concentrated around them compared to N atoms. We observe an apparent electron sharing between the two N atoms, manifesting the N–N coupling due to the presence of the catalytic surface. A similar, but weaker, coupling exists between the O atoms of the dinitrosyl. The absence of bonding charge between the N atoms of the adsorbate and the surrounding terminal O atoms implies a repulsion between them. It is this repulsion that leads to the attraction between the N atoms.

VI. DISCUSSION

The reactions leading to dinitrosyl formation, starting either with gas phase NO or with adsorbed nitrosyl, are summarized in Table III. Although the adsorption of two gas NO molecules to form a dinitrosyl is exothermic by 0.90 eV/molecule (this number is the average between the two characteristic geometries of the dinitrosyl discussed before), the process is expected to have a large energy barrier due to the repulsion of the NO molecules, which, having an electrical dipole moment, would prefer to have an antiparallel configuration. The combination of two adsorbed nitrosyls is also rejected as a mechanism for dinitrosyl formation, as the vacancy left behind makes the process energetically costly. Indeed, as shown in Table III, this reaction is endothermic by more than 2 eV/molecule. The alternative is to fill the O vacancy by an O from the environment. In this case, the dinitrosyl formation is exothermic by 0.81/0.91 eV/molecule. This process, being of the opposite of the NO adsorption, would involve the same transition state and consequently requires overcoming almost the same energy barrier.

A lower energy barrier, with almost the same energy gain, is possible when a gas-phase NO molecule binds to an already adsorbed one (last reaction of Table III). The energy barrier for this case has to be lower than in the previous one, since this process involves no breaking of bonds, while the terminal oxygens of MoO₃ surrounding the adsorbed NO will attract the N atom of the gas-phase NO. The calculated lowest energy, together with the expected low barrier, support the presumption that this is the dominant dinitrosyl formation mechanism.

Combining the previous results, the proposed mechanism for the reduction of NO is described in the following series of reactions:

\[
2\text{NO}(g) \rightarrow \text{NO}(g) + \text{NO}(a) + \frac{1}{2}\text{O}_2 + 0.03 \text{ eV}
\]

\[
\rightarrow (\text{NO})_2(a) + \frac{1}{2}\text{O}_2 + 0.87 \text{ eV}
\]

\[
\rightarrow \text{N}_2 + \text{O}_2 + 1.00 \text{ eV}
\]

A gas NO molecule is exchanged with a MoO₃(010) terminal O, and the system lowers its energy by 0.03 eV. Alternatively, as mentioned in Sec. IV, a vacancy could be created by the reaction of the surface with some other gas-phase molecule; in that case the products of the reaction would not be necessarily include O₂. Another NO molecule binds to the already adsorbed one, lowering the energy of the system by about another 0.84 eV. The next step is either desorption of the two O atoms first (as O₂) followed by desorption of the two N atoms (as N₂), or desorption of one O atom first and then of the N₂O molecule. In both cases, an O atom fills the O vacancy that is left behind so that the catalyst is left unchanged at the end of the process. The final state of the system, with N₂ and O₂ molecules is 20.190 eV lower in energy than the initial state of two NO molecules. The contribution of the catalyst in the process is twofold: first, it can reduce the barrier for NO reduction and, second, it makes it much more probable for two NO atoms to come close to each other and react.

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