DFT-D3 Study of Molecular N$_2$ and H$_2$ Activation on Co$_3$Mo$_3$N Surfaces

Constantinos D. Zeinalipour-Yazdi,* ‡ Justin S. J. Hargreaves,‡ and C. Richard A. Catlow* †

1Kathleen Lonsdale Materials Chemistry, Department of Chemistry, University College London, London, WC1H 0AJ, United Kingdom
2WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, United Kingdom

ABSTRACT: Cobalt molybdenum nitride (Co$_3$Mo$_3$N) is one of the most active catalysts for ammonia synthesis, although the atomistic details of the reaction mechanism are currently unknown. We present a dispersion-corrected (D3) DFT study of the adsorption and activation of molecular nitrogen and hydrogen on Co$_3$Mo$_3$N-(111) surfaces to identify possible activation sites for ammonia synthesis. H$_2$ was found to adsorb both molecularly on the Mo$_3$N framework and dissociatively on Co$_8$ clusters or Mo$_3$ clusters that were exposed due to N-vacancies. We find that there are two possible activation sites for N$_2$, where both N$_2$ and H$_2$ can coadsorb. The first is a Mo$_3$ triangular cluster that resides at 3f nitrogen vacancies, and the second is a surface cavity where N$_2$ is activated by a Co$_8$ cluster, the second being a more efficient activation site. N$_2$ was found to adsorb in three adsorption configurations: side-on, end-on, and an unusual tilt end-on (155°) configuration, and the existence of these three adsorption configurations is explained via MP2 calculations and the sphere-in-contact model.

1. INTRODUCTION

Co$_3$Mo$_3$N when synthesized using the procedure patented by Topsoe is known to be active for ammonia synthesis at 400 °C and elevated pressures using a 3:1, H$_2$:N$_2$ mixture. Indeed, Co$_3$Mo$_3$N when doped with Cs is one of the most active catalysts for ammonia synthesis, with turnover-frequencies (TOF) that are remarkably high compared to graphite-Krevelen (MvK) chemistry and that lattice nitrogen may act in suggested that ammonia synthesis may proceed via Mars–Topsøe mechanism can also proceed via MvK type surface chemistry at low temperatures as there is a large number of nitrogen vacancies (∼10¹⁵ cm⁻²), which can activate N$_2$ by weakening of the triple bond. N-vacancies were also found to participate in the mechanism for the electrochemical reduction of ammonia on VN and ZrN and in the two-step solar-energy driven ammonia synthesis on metal nitrides. Here, we extend the earlier study by investigating the adsorption at every possible site compared to the adsorption of molecular hydrogen.

The rest of the paper has the following structure: first we establish the calculation parameters that reproduce well the electronic structure of Fe$_3$Co$_3$..Mo$_3$N, where x = 0, 1, 2 and 3; next we describe the method for generating slabs of Co$_3$Mo$_3$N-(111) surfaces and apply the calculation parameters to address the question of hydrogen and nitrogen adsorption and activation on Co$_3$Mo$_3$N with and without defects. Finally we explain the various bonding configurations of N$_2$ via molecular orbital (MO) calculations and the sphere-in-contact model.

2. COMPUTATIONAL METHODS

2.1. Methodology. Spin-polarized periodic planewave DFT calculations have been performed with the VASP 5.3.5 code using the revPBE and a 650 eV cutoff for the planewave

Received: May 28, 2016
Revised: August 23, 2016
Published: August 24, 2016

DOI: 10.1021/acs.jpcc.6b04748
expansion. A detailed description of the computational methodology for the plane-wave calculations can be found in ref 13, in which it was found that among various GGA and hybrid-GGA XC functionals, the revPBE yields accurate (to within 1%) bond dissociation enthalpies for N2(x). Here, we further test how well this function can perform in modeling correctly the electronic structure in a homologous series further test how well this functional can perform in modeling the electronic structure in a homologous series of alloys; we note that the revPBE functional, which is implemented in the Gaussian09 code (rev D.01).21 The basis performed within restricted density functional theory (DFT) forces and the root-mean-square (RMS) forces were less than to fully relax the cluster-adsorbate system, the surface and the adsorbate separately. The second was by performing a single point energy calculation with the D3-correction at the minimum energy structure obtained from an optimization without the correction (ΔE_{\text{ads,D3static}}). We find that the latter can lead to large errors with respect to the adsorption energies of hydrogen, which was overestimated by 35% in some cases and have therefore applied the former approach.

Molecular calculations for the electronic structure of N2 were performed within restricted density functional theory (DFT) implemented in the Gaussian09 code (rev D.01).21 The basis set used was the correlation-consistent polarized valence double-ζ abbreviated as cc-pVDZ.22 Stationary states were confirmed by the absence of imaginary frequencies in the vibrational analysis. The convergence criteria for the maximum forces and the root-mean-square (RMS) forces were less than 0.01 eV/Å and 0.001 eV/Å, respectively.

2.2. Choice of XC-Functional for Fe3Mo3N. We find that the choice of exchange-correlation (XC) functional is critical when addressing the chemistry of N2/H2 with Fe_{3-x}Co_{x}Mo3N, where x = 0, 1, 2, and 3. Although it has been shown for solids that hybrid XC functionals HSE06 and PBE0 give better results for calculating lattice parameters, bulk moduli and more importantly formation enthalpies, for cobalt and iron molybdenum nitrides and their alloys; we note that the revPBE functional, which is computationally far less demanding than PBE0 and HSE03/06 can yield an accurate description of the electronic structure of the material under study. Furthermore, it does not overestimate the bandgap by overestimation of the exchange splitting known for the hybrid functional PBE0.23 It has been suggested that the HSE06 functional greatly improves the computer time and resource requirements mostly due the faster convergence of the total energy with respect to k-point mesh, as the bare unscreened exchange operator requires a 12 × 12 × 12 mesh equivalent to a 6 × 6 × 6 mesh for the HSE06 functional.23 However, we found that the latter underestimated by 38 kJ/mol the bond dissociation enthalpy of N2(g), ΔG_0(N−N). Therefore, we have tested the remaining XC-functionals commonly used for solids, PBE, PW91, revPBE, and PBEsol with respect to their accuracies in predicting the lattice constant of Fe_{3-x}Co_{x}Mo3N, where x = 0, 1, 2, and 3 (see Table 1). These alloys contain also iron which makes possible the testing of the computational methodology on other elements for which crystallographic data are available.23–27 Our calculations are based on full optimization of unit cell dimensions and atom positions and the reported mean-average-percent-error (MAPE) value, which indicates to within which percentage the experimental values, are reproduced. The calculated values were compared to two sets of experimental lattice constants: the first comprised solely of PND data obtained at 4.2K (Exp1) and the second based on combined XRD and temperature-dependent magnetic susceptibility measurements (Exp2). In both sets, we obtained the same trend with respect to the average-MAPE calculated at each functional, which was found to be PBE < revPBE < PW91 < PBEsol. In particular, according to Table 1, an average MAPE of 0.30–0.36% was found for PBE: both revPBE and PW91 gave values of about 0.5–0.6% and PBEsol gave higher average MAPE, of the order of 2%. The results show that with the use of a plane-wave code the lattice parameter can be estimated very well both with the PBE and the revPBE functional, which are also computationally less expensive than some of the hybrid GGA functionals tested.

In an earlier account of bond dissociation enthalpy (BDE) of N2 with the use of various XC functional, the % error for the revPBE was found to be the lowest among various GGA and hybrid GGA functionals.23 In particular, we found that the % error was for revPBE = 0.2 < B3LYP = 1.7 < PBE0 = 3.5 < HSE06 = 4.1 < PBE = 4.9 < PW91 = 7.0. Therefore, all subsequent calculations have been performed with the revPBE functional, which can yield more accurate barrier heights according to the calculated BDE of the N≡N bond.

3. RESULTS AND DISCUSSION

3.1. Surface Models of Co3Mo3N. We have modeled the surface of Co3Mo3N using a 2 × 2 supercell slab with trigonal symmetry belonging to the space group P3m1 (164), where a = b = 7.7972 Å, c = 30 Å, α = β = 90°, and γ = 120°. This was generated from a cubic unit cell with the η-carbide Fe3W5C structure belonging to the space group Fd3m (227), where a = b = c = 3.937 Å, α = β = γ = 90°, a = b = c = 3.937 Å, α = β = γ = 90°, and γ = 120°.
Various surface compositions of Co$_3$Mo$_3$N-(111) surfaces found

- **A**: CoMo$_{0.9}$N$_{2.1}$, N: 6f
- **B**: CoMo$_{1.2}$N$_{0.4}$, N: 5f
- **C**: CoMo$_{1.0}$N$_{0.4}$, N: 3f
- **D**: CoMo$_{0.8}$N$_{0.2}$, N: 6f
- **E**: CoMo$_{0.7}$N$_{0.3}$, N: 3f
- **F**: CoMo$_{0.8}$N$_{0.3}$, N: 3f

**Figure 1.** 2 x 2 surface supercells of Co$_3$Mo$_3$N showing surface terminations of different composition in cobalt molybdenum nitride (111) surfaces. Note that only four out of the six surface compositions expose surface nitrogen (i.e., 5f or 3f). Two surfaces only have subsurface nitrogen (i.e., 6f).

**Figure 2.** Symmetry unique sites for molecular hydrogen adsorption on Co$_3$Mo$_3$N surface C, in the presence of a nitrogen vacancy (site 1 and 2) in (a) top view and (b) perspective view.

$b = c = 11.0270$ Å and $\alpha = \beta = \gamma = 90^\circ$.\textsuperscript{29} We note that the (111) surface of the cubic unit cell (Fd$\overline{3}$m) is the (001) surface of the trigonal unit cell (P$\overline{3}$m1), which was further studied as it has the highest density of Co$_8$ clusters embedded in a molybdenum nitride (Mo$_3$N) framework. In the case of a bifunctional mechanism, this surface would have the largest density of active sites. For the rest of the paper, we refer to this "(111)-surface" simply as "surface". Note that the actual 2 x 2 supercell used for these periodic slab calculations was shifted by a/2 and along a and by b/2 along b and had a nitrogen vacancy at the position indicated by a yellow circle in Figure 1. The slabs were generated by applying a scanning algorithm to scan the bulk in 0.1 Å increments and generate centro-symmetric slabs of thickness <1 nm for computational efficiency. A top view of these slabs along the c direction is shown in Figure 1 that shows the composition of six distinct surfaces generated, of which four had surface nitrogen (i.e., B, C, E, and F) and two had only a MoCo exposed phase (i.e., A and D) with subsurface nitrogen. The subsurface nitrogen is a 6-fold bound nitrogen (6f) to Mo atoms, whereas surfaces C, D, and F had entirely 3f nitrogens, and one surface (B) had 5f nitrogens. The nitrogen vacancy formation energies (VFE) and concentrations have been previously calculated, and the latter was found to be on the order of $10^{13}$ per cm$^2$ at ambient conditions.\textsuperscript{13} We have
evaluated the surface composition in these slabs and found that it significantly differs among these thin films. It is interesting to note that the surface with the highest surface nitrogen concentration, C had a very low composition of nitrogen based on the normalized stoichiometric coefficient (s.c.) of nitrogen, having set the s.c. of cobalt to 1. These compositions were found to be A = CoMo0.9N_0.1, B = CoMo0.8N_0.2, C = CoMo0.7N_0.3, D = CoMo0.6N_0.4, E = CoMo0.5N_0.5, and F = CoMo0.4N_0.6. For example surface A, which had a complete absence of exposed surface nitrogen, had the highest stoichiometric coefficient for nitrogen (i.e., N_s.c.). This suggests that the exact surface composition of very thin layers of this material may have to be evaluated by topographic techniques, e.g., via scanning probe microscopies that are currently absent in the literature. In an earlier DFT study, with the same methodology used here, we proposed that surface C is the most active surface for Mars–van Krevelen type chemistry for ammonia synthesis. This choice was based on two kinetic factors and an energetic factor: (i) the density of sites that can activate N_2 (i.e., N-vacancies), (ii) which surface had the most exothermic adsorption energies for N_2 adsorption, and (iii) the surface formation energies (E_f), which were calculated for the four surface compositions that had exposed surface nitrogen. As the calculation of surface stabilities is not possible for Co_3Mo_3N, we continue with surface C for calculating the coadsorption of N_2/H_2 on Co_3Mo_3N.

3.2. H_2 Adsorption and Activation on Co_3Mo_3N.

Various phases of atomically adsorbed hydrogen have been observed via scanning-tunnelling microscopy (STM) on Co nanoparticles grown on Cu(111). In a recent DFT study, the adsorption energy of H_2 was found to be roughly proportional to the percentage of H_2 dissociation. Furthermore, the stronger adsorption energy for H_2 results in a molybdenum atom that was adjacent to a nitrogen-vacancy site (N_vac) with an adsorption energy of ~67 kJ/mol but with only a small activation of the H–H bond.

Site 2 was found to dissociatively chemisorb H_2, where it was found to be bound to a molybdenum atom at a nitrogen vacancy site. This site had the largest % activation (i.e., 41%) for molecular hydrogen; sites 3–5 in which hydrogen was adsorbed on a molybdenum atom on the MoN_3 framework with a moderate adsorption energy of ~30 to ~68 kJ/mol due to the less metallic character of the MoN_3 framework. The strongest adsorption energy for H_2 was found on sites 6–7, which corresponds to a corner atom of the Co_8 nanoclusters denoted as Co_8-top with adsorption energy of ~127 and ~110 kJ/mol, respectively. At these sites, the H–H bond was also found to be considerably activated (i.e., ~23–24%). These results indicate that the Co_8 clusters will be saturated with molecular hydrogen at low temperatures under conditions where both N_2/H_2 are available in the feedstream. Interestingly we find that at site 8, H_2 will generally not adsorb at low-T based on the D3-corrected adsorption energy of just 21 kJ/mol, and it is the only site on the Co_3Mo_3N surface that will not be occupied by hydrogen when it is coadsorbed with N_2. Therefore, we consider site 8 as free under conditions of competitive adsorption with N_2 at low temperatures (e.g., T < 200 °C).

3.3. N_2 Adsorption and Activation on Co_3Mo_3N.

The adsorption of N_2 over a range of surfaces has been studied using various surface analytical probes extensively. Both physisorbed and chemisorbed states are identified using a combination of electron spectroscopy and thermal desorption techniques. According to this report and earlier LEED experiments, N_2 can chemisorb side-on and end-on on the surfaces of certain metals (e.g., Ni, Fe, Ru, and W). In this study, we find that apart from these two adsorption configurations, N_2 can also adsorb in a tilt end-on configuration on Co_3Mo_3N shown in Scheme 2. This is a well-defined adsorption configuration with a tilt angle equal to 155° in which the dihedral d(Co–Mo–N–N) of this bond is found to be 0°.

Angle resolved photoemission spectra have identified two phases of N_2 adsorbed to Fe(111) surfaces (γ-phase and α-phase). In the first, N_2 is adsorbed perpendicularly, and in the latter in a strongly inclined configuration, where N_2 was described to form two covalent bonds with Fe atoms. A Co(2 × 2)-N/Fe(100) structure was found to form on Fe(111) and Fe(110) surfaces, whereas two side-on (α and α′) and two end-on (β and γ) adsorbed states have been found via periodic DFT calculations for molecular N_2 adsorption on Fe(111). Two
adsorption configurations for molecular nitrogen have been previously identified as side-on and end-on, based on an extensive collection of surface analytical studies. Side-on and end-on adsorbed configurations for N_2 when it is adsorbed to nickel surfaces have also been found, where the end-on adsorption occurs either through a single surface atom on Ni(110) surfaces or in a tilt end-on configuration through two surface atoms on Ni(110) surfaces. An end-on adsorbed configuration of N_2 as well as CO, which is isoelectronic, was found via X-ray emission spectroscopy (XES) and DFT calculations on Ni(110). An end-on adsorbed configuration for N_2 has been found on cobalt clusters of the form Co_n(N_2)^*, where n = 8-17 using infrared photon dissociation (IRPD) spectroscopy and DFT calculations of the stretching frequency of the N–N bond.

The 32e and 16d Wyckoff sites of the Co_8 in the bulk, have been denoted as Co_8-top and Co_8-ads for the surface slabs, respectively. Percent activation is defined as \[|r(H_2,g) - r(H_2,ads)| \times 200/|r(H_2,g) + r(H_2,ads)|\].

On the surface of Co_3Mo_3N (i.e., surface C), we have identified three adsorption configurations for N_2, which are shown in Scheme 2. For the eight adsorption sites, we placed N_2 either side-on or end-on at every site shown in Figure 3 and let it optimize without any restrictions. The adsorption energies for N_2 without (\(\Delta E_{N_2}\)) and with (\(\Delta E_{N_2,relax-D3}\)) the inclusion of dispersion interactions via the DFT-D3 method and the optimized structure of the adsorbates (i.e., \(r_{(H-H)}\) and \(r_{(M-M)}\)) are presented in Table 3. The side-on configurations stayed either side-on or became a tilt end-on configuration during relaxation. This change in adsorption configurations was not observed for the end-on configuration, which remained end-on even after relaxation. This indicates that there is barrier for the end-on to side-on transformation. Adsorption at some sites would activate nitrogen, but dissociation such as in the case of H_2 was not observed, in accord with the large bond dissociation enthalpy of N_2 (i.e., 946 kJ/mol).

The various adsorption sites found had the following characteristics: site 1 the nitrogen was adsorbed in a tilt end-on configuration to a molybdenum atom that was adjacent to a nitrogen-vacancy site (N_vac) with an adsorption energy of \(-59\) kJ/mol but with only a small activation of the N–N bond. Site

![Figure 3](image-url)

---

**Table 2. Adsorption Energy (\(\Delta E\)) of H_2 Adsorbed to C Surface of Co_3Mo_3N: H–H Bond Length (\(r(H-H)\)), M–N Bond Length (\(r(M-N)\)); Tilt Angle (\(a(M-H-M)\)); Adsorption Site Composition and % Elongation for Side-On Adsorption at Various Distinct Adsorption Sites on 2 \(\times\) 2 Co_3Mo_3N with a Slab Composition of CoMoN_{0.4}**

<table>
<thead>
<tr>
<th>property</th>
<th>site 1</th>
<th>site 2</th>
<th>site 3</th>
<th>site 4</th>
<th>site 5</th>
<th>site 6</th>
<th>site 7</th>
<th>site 8</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E_{H2})</td>
<td>-78.04</td>
<td>-87.60</td>
<td>-59.22</td>
<td>-64.47</td>
<td>-124.93</td>
<td>-124.93</td>
<td>49</td>
<td>kJ/mol</td>
<td></td>
</tr>
<tr>
<td>(\Delta E_{H2,relax-D3})</td>
<td>-67.99</td>
<td>-96.29</td>
<td>-32.06</td>
<td>-55.23</td>
<td>-121.27</td>
<td>-110.99</td>
<td>21</td>
<td>kJ/mol</td>
<td></td>
</tr>
<tr>
<td>(\Delta E_{H2,static-D3})</td>
<td>-126.50</td>
<td>-126.50</td>
<td>-72.48</td>
<td>-91.22</td>
<td>-128.93</td>
<td>-110.99</td>
<td>21</td>
<td>kJ/mol</td>
<td></td>
</tr>
<tr>
<td>(r(H-H))</td>
<td>0.820</td>
<td>1.041</td>
<td>0.768</td>
<td>0.809</td>
<td>0.807</td>
<td>0.910</td>
<td>0.917</td>
<td>0.800</td>
<td>Å</td>
</tr>
<tr>
<td>(r(M-N))</td>
<td>0.79</td>
<td>0.72</td>
<td>0.85</td>
<td>0.79</td>
<td>0.80</td>
<td>0.73</td>
<td>0.73</td>
<td>0.87</td>
<td>Å</td>
</tr>
<tr>
<td>type</td>
<td>side-on</td>
<td>side-on</td>
<td>side-on</td>
<td>side-on</td>
<td>side-on</td>
<td>side-on</td>
<td>side-on</td>
<td>side-on</td>
<td></td>
</tr>
<tr>
<td>bound to</td>
<td>Co_8</td>
<td>Co_8</td>
<td>MoN_3</td>
<td>MoN_3</td>
<td>MoN_3</td>
<td>MoN_3</td>
<td>Co_8-top</td>
<td>Co_8-top</td>
<td></td>
</tr>
<tr>
<td>H_2 activation</td>
<td>12</td>
<td>41</td>
<td>4</td>
<td>9</td>
<td>9</td>
<td>23</td>
<td>24</td>
<td>8</td>
<td>%</td>
</tr>
</tbody>
</table>

---

**Scheme 2. Simplified Schematic Showing Side-On, End-On, and Tilt End-On Coordinations of N_2 Bound to the Co_3Mo_3N Surface**

---

**Figure 3. Symmetry unique adsorption sites for molecular nitrogen on Co_3Mo_3N surface C in the presence of a nitrogen vacancy (site 1 and 2) in (a) top view and (b) perspective view. Note that all adsorption sites are shown in one unit cell; however, the simulations results tabulated in Table 2 contained only one adsorbed nitrogen per 2 \(\times\) 2 unit cell.**
2 was found to activate \( N_2 \) where it was bound end-on at the 3-fold hollow generated by the nitrogen vacancy. This site had the second largest % activation (i.e., 11%) for molecular nitrogen. Site 3 \( N_2 \) was adsorbed in an end-on configuration on the Mo\( _3 \)N framework with a weak adsorption energy (1.5 kJ/mol) due to the less metallic character of the Mo\( _3 \)N framework. Site 4–5 \( N_2 \) adsors in a tilt end-on at the 32e Wycko site of the (Co\( _{8\text{top}} \)) configuration with a 4–5% activation of the N–N bond and an adsorption energy of −30 to −41 kJ/mol. Site 6–7 \( N_2 \) adsorbs in a side-on at the 32e Wycko site (Co\( _{8\text{top}} \)), with a 4–5% activation of the N–N bond. Interestingly we find a surface cavity on surface C of Co\( _3 \)Mo\( _3 \)N (site 8), at which there is the largest activation of N–N bond, 21%. This % activation is even larger than the activation that we have found at 5f sites on N\( _2 \) adsorbs in a calculated with MP2/cc-pVTZ the molecular orbitals (MOs) of 58.9 kJ/mol. To summarize, two activation sites for N\( _2 \) have been found (i) the second largest % activation of the N bond, 21%. This % activation is defined as \( [r(N_2, g) - r(N_2, \text{ads})] \times 200 /[r(N_2, g) + r(N_2, \text{ads})] \).

The 32e and 16d Wycko sites of the Co\( _8 \) in the bulk, have been denoted as Co\( _{8\text{top}} \) and Co\( _{8\text{side}} \) for the surface slabs, respectively. The percent activation is defined as \( [r(N_2, g) - r(N_2, \text{ads})] \times 200 /[r(N_2, g) + r(N_2, \text{ads})] \).

<table>
<thead>
<tr>
<th>property</th>
<th>site 1</th>
<th>site 2</th>
<th>site 3</th>
<th>site 4</th>
<th>site 5</th>
<th>site 6</th>
<th>site 7</th>
<th>site 8</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E_{\text{ads}} )</td>
<td>−58.9</td>
<td>−19.6</td>
<td>59.8</td>
<td>−33.6</td>
<td>−44.3</td>
<td>−22.1</td>
<td>−18.7</td>
<td>79.3</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>( \Delta E_{\text{ads,relax}} )</td>
<td>−58.9</td>
<td>−48.8</td>
<td>1.5</td>
<td>−29.9</td>
<td>−41.3</td>
<td>−38.2</td>
<td>−13.6</td>
<td>40.2</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>( r(N-N) )</td>
<td>1.166</td>
<td>1.244</td>
<td>1.130</td>
<td>1.173</td>
<td>1.163</td>
<td>1.166</td>
<td>1.173</td>
<td>1.357</td>
<td>Å</td>
</tr>
<tr>
<td>( a(M-N-N) )</td>
<td>154</td>
<td>176</td>
<td>175</td>
<td>152</td>
<td>158</td>
<td>75</td>
<td>73</td>
<td>71</td>
<td>Å</td>
</tr>
<tr>
<td>( r(M-N) )</td>
<td>1.573</td>
<td>1.930</td>
<td>2.398</td>
<td>1.820</td>
<td>1.754</td>
<td>2.001</td>
<td>1.971</td>
<td>1.928</td>
<td>Å</td>
</tr>
</tbody>
</table>

Table 3. Adsorption Energy (\( \Delta E_{\text{ads}} \)) of \( N_2 \) Adsorbed to C Surface of Co\( _3 \)Mo\( _3 \)N, N–N Bond Length (\( r(N-N) \)), M–N Bond Length (\( r(M-N) \)), Tilt Angle (\( a(M-N-N) \)), Adsorption Site Composition, and % Elongation for Side-on Adsorption at Various Distinct Adsorption Sites on 2 × 2 Co\( _3 \)Mo\( _3 \)N (Surface C)

Figure 4. Molecular orbitals and their corresponding energies for \( N_2 \) calculated at MP2/cc-pVDZ level of theory, as well as how they correlate to the various adsorbed configurations of \( N_2 \).

The Journal of Physical Chemistry C

DOI: 10.1021/acs.jpcc.6b04748

emission spectroscopy (XES) studies. CO adsorbed in a tilt configuration has been previously found on Ag\(_n\) (\(n = 1\) to 7), which was rationalized on the basis of better orbital overlap of tilt-CO with Ag\(_n\)-HOMO of \(\sigma\)-symmetry and of the linear end-on CO with Ag\(_n\)-HOMO of \(\pi\)-symmetry.\(^{49}\) Furthermore, a tilt-CO was also found as a results of CO–CO repulsions\(^{50,51}\) or adsorption at 4-fold hollow sites.\(^{52}\) There have been many computational studies of the doping, support and NP-size effects on CO adsorption on various metal and their oxides\(^{53–56}\) and as elementary reaction steps in catalytic reactions.\(^{60–62}\) In a recent combined DFT and experimental study of the catalytic CO oxidation using bimetallic M\(_{\text{Au25-Sc6H4Ph}}\) clusters, where \(M = \text{Cu, Au, Ag}\) the following trend Cu > Au > Ag was found and interpreted as a result of a stronger metal-CO interaction in metals with a smallest covalent radius.\(^{63}\) Based on these earlier studies and the results found here, we rationalize that the \(\pi\)-back-donation of electron density into the LUMO of both N\(_2\) and CO is expected to result in a linear end-on adsorption.\(^{64}\) The tilt end-on adsorption configuration of N\(_2\) on Co\(_3\)Mo\(_3\)N has not been previously reported and is shown in Scheme 2. This is a well-defined adsorption configuration with a tilt angle equal to 155° in which the dihedral \(d(\text{Co–Mo–N–N})\) of this bond is found to be 0. In the following section, we provide evidence that there are two bonding interactions that take place based on the sphere-in-contact model.\(^{65}\) We have taken literature values for the atomic radius of the elements participating in the bonding and drawn to scale a sphere-in-contact model of the tilt end-on adsorption configuration for N\(_2\) on Co\(_3\)Mo\(_3\)N. This is depicted in Figure 5.

![Figure 5. Sphere-in-contact model of tilt end-on adsorption configuration for N\(_2\) on Co\(_3\)Mo\(_3\)N.](image)

From the optimized structures presented in Table 2, we find that the tilt angle ranges between 152 and 158° with an average value at 155°. We have used the sphere-in-contact model to provide an explanation of the bonding in the tilt end-on configuration. In this model, each element is represented by its atomic radius. The atomic radius of nitrogen we can estimate from our DFT calculations (N: 58.4 pm) based on the average bond length of N\(_2\) for the tilt end-on configuration, in excellent agreement with the double bond atomic radius obtained by fitting a set of atomic radius data of various elements (60 pm).\(^{66}\) For the atomic radius of molybdenum and cobalt, we used literature values of 190 and 152 pm, respectively.\(^{67}\) If we draw the bonding via a sphere-in-contact model as shown in Figure 5, we find that for a tilt angle of 155°, the spheres are in perfect contact, which indicates the presence of covalent bonding interactions, and that there is bonding both from the 3\(\pi\)g (HOMO–1) along the molecular axis of N\(_2\) and the 1\(\pi\)g (HOMO) perpendicular to the molecular axis of N\(_2\). This orientation is such that it would additionally undergo interactions between filled d-states of the metal and antibonding 1\(\pi\)*g MO of N\(_2\). The small percentage activation of the N–N bond indicates a potential bonding mechanism where \(\pi\)-back-donation and a tauochronous \(\sigma\)- and \(\pi\)-repulsion are present, which results in this unusual tilt end-on adsorbed configuration of N\(_2\).

**CONCLUSIONS**

We present a dispersion-corrected DFT study of the adsorption and activation of molecular nitrogen and hydrogen on cobalt molybdenum nitride (111) surfaces to identify possible activation sites for ammonia synthesis. H\(_2\) was found to adsorb both molecularly on the Mo\(_3\)N framework and dissociatively on Co\(_8\) clusters or Mo\(_3\) clusters that were exposed due to N-vacancies. N\(_2\) was found to adsorb side-on, end-on, and in an unusual tilt end-on configuration, which is rationalized via MO diagrams and the sphere-in-contact model. We find that there are two possible activation sites for N\(_2\). The first is a Mo\(_3\) triangular cluster that resides at 3\(f\) nitrogen vacancies and the second is a surface cavity where N\(_2\) is activated by the inner tetrahedral atom of the Co\(_8\) cluster, the second being a more efficient activation site and a particular activation sites exposed only in Co\(_3\)Mo\(_3\)N surfaces with a surface composition of CoMoN\(_{0.4}\).

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: c.zeinalipour-yazdi@ucl.ac.uk; Tel: +44 207-679-0312.*

*E-mail: c.r.a.catlow@ucl.ac.uk; Tel: +44 207-235-2818.*

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge EPSRC funding (EP/L026317/1, EP/L02537X/1). Via our membership of the UK’s HPC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202/1); this work used the ARCHER UK National Supercomputing Service (http://www.archer.ac.uk).

**REFERENCES**


The Journal of Physical Chemistry C


