

CO Adsorption on Molybdenum Nitride's γ -Mo₂N(100) Surface: Formation of N=C=O Species? A Density Functional Study

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To gain insight into the electronic surface properties of γ -Mo₂N(100) and the CO chemisorption, density functional calculations have been undertaken on periodic surface models using the generalized gradient approximation for the exchange-correlation functional. Structure relaxation of γ -Mo₂N(100) has been performed for different models depending on the surface stoichiometry (Mo/N ratio, mimicking the nitridation effect) or composition (O adatom, mimicking the passivation effect). The reaction γ -Mo₂N(100) + X₂(g) → γ -Mo₂N(100)-X, with X = N and O, is calculated to be exothermic. This suggests that stoichiometric (100) surfaces containing 4-fold vacancy sites are unstable with respect to the dissociative adsorption of N₂ and O₂ molecules. The chemisorption sites of CO and the associated CO vibrational frequencies have been determined for the Mo₂N(100)-X/CO surfaces. On a stoichiometric (100) surface, a μ_4 -bonding mode of CO is localized on the potential energy surface with the same binding energy as the ones calculated for the on-top metallic sites ($\Delta H_{\text{ads}} \sim -1.4$ eV) while the CO binding on nitrogen adatoms is an endothermic process with an adsorption enthalpy of +0.23 eV. For a full nitrogen coverage or a nitrided (100) surface, an exothermic reaction is now calculated ($\Delta H_{\text{ads}} = -0.76$ eV) for the formation of a chemisorbed N=C=O species. For the on-top Mo and N_{surf} sites, the associated CO frequencies values depend on the chemical nature of the surface rather than on the coordination number of the metallic atoms. Finally, in the reaction of gas-phase CO with surface nitrogen atoms an Eley–Rideal mechanism may be operational with an activation barrier of 1.5 eV.

Introduction

Since the pioneering work of Boudart and co-workers,¹ transition metal nitride based catalysts have been the subjects of numerous experimental investigations motivated by their catalytic properties.² Especially, γ -Mo₂N compounds seem to have good activity (NH₃ synthesis)^{2b, g} or selectivity (ortho-para hydrogen inversion)^{2b} and good resistance to poisoning during the hydrotreating reactions (HDN, HDS)^{2a–e} of low-quality petroleum feedstocks. However, there still remain many unanswered questions concerning the precise nature of the surface active sites. The study of molecules adsorbed on γ -Mo₂N surfaces may give some insights into the local structural properties of the catalyst. In this context, recent experimental results on CO adsorption suggest that active nitrogen surface sites are present on fresh supported γ -Mo₂N catalyst leading to the unusual reaction of CO with surface nitrogen atoms to form a chemisorbed NCO species.³ These findings and FT-IR interpretations leave several questions open: (i) What is the local structural aspect of the chemical surface? (ii) Why has the catalytic surface to be nitrided to allow for a reaction of N_{surf} and CO? (iii) What is the mechanism for the CO + N_{surf} reaction?

The objective of the present work is to study the adsorption of CO on γ -Mo₂N(100) in order to answer to the above

questions and therefore to get enlightenment on the local catalytic structure by means of density functional calculations on periodic systems. The model is considered in the next section.

Surface Modeling and Computational Aspects

All periodic calculations are based on density functional method and are performed using the Vienna ab initio simulations program (VASP)⁴ within the framework of the generalized gradient approximation (GGA) of Perdew et al.⁵ This method applies a plane-waves basis and optimized ultrasoft pseudo-potentials. For a detailed description of the theory, we refer to the papers by Kresse et al.⁴ Typical cutoff energies for the plane wave expansion of the eigenstates can be as low as 400 eV. A spin-restricted approach is used for all surface models since polarization effects were found to be negligible. For atoms and open-shell molecules such as NCO and O₂, a spin-unrestricted approach is used. In cubic γ -Mo₂N, the metal atoms form a fcc arrangement and the nitrogen atoms occupy statistically half of the octahedral interstitial sites. For bulk γ -Mo₂N, the calculated equilibrium lattice parameter of $a = 4.21$ Å is in good agreement with the experimental values of 4.163 Å given in the JCPDS tables and 4.20 Å determined by other authors.⁶ The calculated Mo–Mo and Mo–N distances are equal to 2.97 and 2.11 Å, respectively. Regarding the surface structure, there are no experimental data available. In this work, we have considered the (100) surface as the {100}_{Mo₂N} planes are parallel to the platelets of γ -Mo₂N crystallites.^{1,6} Cleavage parallel to the (100)

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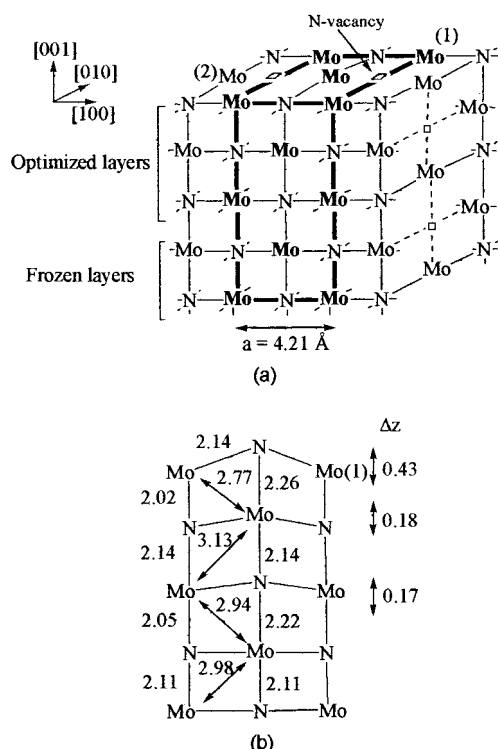


Figure 1. (a) γ -Mo₂N(100) 1 × 1 surface model. Half of the octahedral sites in the fcc Mo structure are vacant (i.e. the 4-fold hollow sites). (b) Relaxed γ -Mo₂N(100) 1 × 1 surface looking at the plane perpendicular to the surface showing the Mo–N–Mo bond alternation. The mean distances between the molybdenum and nitrogen planes in a given layer are indicated by Δz (distances in angstroms).

planes of clean γ -Mo₂N exposes unsaturated Mo and N atoms, and 4-fold-type vacancies are created, namely octahedral sites (see Figure 1a). Therefore, we model the (100) γ -Mo₂N surface with a stoichiometric slab consisting of five monolayers of Mo₂N, resulting in 15 atoms per 1 × 1 unit cell. The two different coordinatively unsaturated metallic sites are shown in Figures 1 and 2, named Mo(1) and Mo(2), which are three- and two-coordinated atoms, respectively. The three first layers are allowed to relax, while the two lower ones are held in their bulk positions. The vacuum spacing between two repeated slabs is set to 12.6 Å. Brillouin zone integration is performed on a grid of 3 × 3 × 1 Monkhorst–Pack special k -points (4 k -points) for a square lattice.⁷ The number of k -points was considered converged when the atomic positions change by less than 0.01 Å in structural optimization. This model is employed as a compromise between computational economy and reasonable accuracy. To mimic the nitrided and passivated surfaces we have considered different models where the 4-fold vacancies, i.e., the octahedral sites on the active surface, are filled with nitrogen or oxygen atoms. Such models are idealized since Mo–AH_x (A = N, O) or Mo–H surface groups may be present. Nevertheless, we believe that they should be a reliable starting model to determine the CO chemisorption sites.⁸ For the sake of comparison, the CO adsorption on hypothetical fcc Mo(100)- $c(2 \times 2)$ ⁹ and cubic (NaCl-type) MoN(100)- $c(2 \times 2)$ ¹⁰ surfaces has been investigated. In the bulk state, the optimized lattice parameters are 3.99 Å for fcc Mo and 4.35 Å for MoN. Bond stretching frequencies are obtained numerically. Internal coordinates second-order derivatives are computed using a least-squares polynomial fit of the total energy and internal forces. Harmonic frequencies are derived using the INTDER95 program.¹¹ We only considered linear deformations of Mo–C–O and Mo–N–C–O species where the surface molybdenum atom

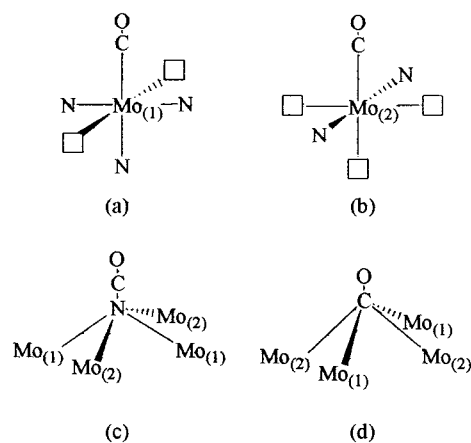


Figure 2. Local coordination modes of CO on clean (100) 1 × 1 surface: (a) on-top Mo(1); (b) on-top Mo(2); (c) on-top nitrogen surface atom, N_{surf}; (d) on 4-fold site, μ_4 -CO. The square symbols correspond to the vacant 4-fold hollow sites which are filled by nitrogen or oxygen atoms for a coverage surface of Mo/X = 1 (X = N, O).

is supposed to be fixed. Polynomials up to order 5 are obtained on a grid. The Mo–C, C–O, and N–C distances are varied using a 0.05 Å step on the interval [−0.10 Å, +0.25 Å] around the computed equilibrium distance. In the NCO case, the interval is restricted to [−0.05 Å, +0.05 Å] for the Mo–N variation. The comparison between the computed values for the free CO molecule ($\omega_e = 2110 \text{ cm}^{-1}$) and NCO radical ($\nu_{\text{asym}} = 1960 \text{ cm}^{-1}$ and $\nu_{\text{sym}} = 1238 \text{ cm}^{-1}$) with experimental data (2169.81, 1921.28, and 1266.63 cm^{-1} , respectively)¹² give some indication on the accuracy of the method used. The maximum deviation of 3% is comparable with DFT molecular or other periodic calculations.¹³ With modification of the number of considered points in the polynomial fit or the order of the polynomial approximation, variations of less than 20 cm^{-1} are obtained for the computed frequencies.

CO Adsorption on Clean γ -Mo₂N(100)

We started with the proper bulk stacking of stoichiometric Mo₂N units. The reconstruction of the 100 surface leads to an energy gain of 0.85 eV. In comparison with the bulk, in-plane Mo–Mo and Mo–N distances do not change significantly (2.95–2.98 and 2.10–2.15 Å, respectively) while the out-of-plane distances vary from 2.77 to 3.13 Å for Mo–Mo bonds and from 2.01 to 2.26 Å for Mo–N bonds. The main structural modifications for γ -Mo₂N relaxation may be seen by looking at the Mo–N–Mo bond alternation along the [001] direction, i.e., z axis (see Figure 1b). The driving force for distorting the Mo–N–Mo chain such as to yield a asymmetric Mo–N---Mo linkages is mainly due to the mixing of metal π bands with bridging ligand $p_\pi(\text{N})$ bands. This leads to a stabilization of the corresponding occupied bands. This Peierls distortion has been already explained by Hoffmann and co-workers for compounds containing M–N–M linkages (M, transition metal).¹⁴

The investigation of CO adsorption on several sites and starting geometries leads to the identification of four minima on the potential energy surface. The corresponding local bonding modes are shown in Figure 2, and the associated parameters are compiled in Table 1. Detailed structural parameters are given in Supporting Information. The most favorable energetic site for CO chemisorption is found to be the 4-fold site, i.e., the octahedral site in the parent fcc structure. The CO molecule is connected to four molybdenum atoms ($\text{Mo–C}_{\text{av}} = 2.27 \text{ \AA}$; C–O = 1.25 Å) with an adsorption enthalpy, ΔH_{ads} , of −1.49 eV. The μ_4 -CO frequency is calculated to be 1486 cm^{-1} , which

TABLE 1: Heats of Adsorption ΔH_{ads} (eV), Optimized Geometries (in Å),^a and Harmonic Vibrational Frequencies (cm⁻¹) for CO as a Function of Chemisorption Sites on Clean Mo₂N(100), Mo₂N(100)-N, Mo₂N(100)-O, Mo₂N(100)-2O,^b fcc MoN(100), and fcc Mo(100) Surfaces^c

| | Mo ₂ N(100) model | | | | | | | | | MoN (100) model | | Mo(100) model |
|-------------------------|-------------------------------|-------|-------|-------------------|--------------|-------|-------|-----------------------------------|-------------------------------|-----------------|-------|-----------------|
| | $\tau_N = 0.5$ | | | | $\tau_N = 1$ | | | $\tau_N = 0.5,$ $\tau_O = 0.5$ | $\tau_N = 0,$ $\tau_O = 1$ | $\tau_N = 1$ | | $\tau_N = 0$ |
| | Mo(1) | Mo(2) | octa | N | Mo(1) | Mo(2) | N | Mo(1) | Mo(1) | Mo | N | Mo |
| | | | | | | | | | | | | |
| ΔH_{ads} | -1.43 | -1.32 | -1.49 | +0.23 | -0.60 | -1.27 | -0.77 | -0.33 | -0.15 | -0.67 | -0.72 | -1.8 1 |
| $d_{\text{Mo}-Y}^d$ | 2.06 | 2.06 | 2.27 | 2.43 | 2.04 | 2.00 | 2.56 | 2.09 | 2.23 | 2.03 | 2.57 | 2.03 |
| | | | 2.28 | 2.59 | | | 2.57 | | | | 2.57 | |
| $d_{\text{C}-\text{O}}$ | 1.16 | 1.16 | 1.25 | 1.18 | 1.16 | 1.16 | 1.18 | 1.15 | 1.15 | 1.16 | 1.18 | 1.17 |
| $d_{\text{N}-\text{C}}$ | | | | 1.24 | | | 1.23 | | | | 1.23 | |
| ν_{CO} | 1994 | 1987 | 1486 | 2228 ^e | 1997 | 1993 | 2206 | 2034 | 2041 | 2011 | 2202 | 1954 |
| ν_{NCO} | | | | 1122 ^f | | | 1241 | | | | 1236 | |
| ν_{S}^g | 416 | 400 | 302 | 165 | 400 | 415 | 190 | 343 | 167 | 417 | 202 | 431 |

^a See also in Supporting Information. ^b The two 4-fold surface sites are occupied by oxygen atoms. ^c τ_N and τ_O are the nitrogen and oxygen coverage in the first layer, respectively. ^d Y = CO or NCO. ^e Antisymmetric stretching for NCO. ^f Symmetric stretching for NCO. ^g Surface-Y vibrational frequency.

reflects a pronounced weakening of the CO bond. To our knowledge, such chemisorbed μ_4 -CO molecules have not been observed experimentally on the Mo₂N catalyst, even if the 4-fold hollow in (100) fcc surface has been suggested as a candidate adsorption site for diatomic molecules on the basis of IR interpretation.¹⁵ The other two lowest energy sites correspond to the usual on-top adsorption of CO on transition metal atoms (Mo-C = 2.06 Å and C-O = 1.16 Å). Their enthalpies of adsorption are -1.43 and -1.32 eV for the Mo(1) and Mo(2) sites, respectively. A parallel may be made with group 8-10 metal surfaces such as Pd(100) for which the on-top CO binding energy is evaluated to be 1.44 eV,¹⁶ illustrating the well-known Pt-like catalytic properties for nitride molybdenum catalysts.^{1,2} At our level of approximations, these three sites are nearly equivalent for CO adsorption; energy differences are smaller than 5 kcal.mol⁻¹. The calculated frequencies reported in Table 1 are very similar for Mo(1) (1994 cm⁻¹) and Mo(2) (1987 cm⁻¹). These values are intermediate between those obtained for CO on the molybdenum (100) surface (ν_{CO} = 1954 cm⁻¹) and the MoN (100) surface (ν_{CO} = 2011 cm⁻¹). Assuming that the difference between the computed and the experimental value obtained for the free CO molecule is transferable, the corresponding scaled frequencies should be around 2050 cm⁻¹ in agreement with the observed band at 2045 cm⁻¹.³ The last characterized site is the N surface atom for which CO adsorption leads to the formation of a chemisorbed NCO species. The calculated ΔH_{ads} corresponds to a slightly endothermic reaction (+0.23 eV), but the linear μ_4 -NCO species is a true minimum. One may conclude that, on clean Mo₂N(100) surface, the formation of NCO species is thermodynamically unfavorable.

Effect of Nitrogen and Oxygen Coverage on CO Adsorption

N₂ adsorption on Mo₂N is known to be dissociative and to form at high temperature a nitrogen-saturated surface, while O₂ exposure leads to the passivation of the surface by creating oxinitride or oxide sublayer(s).² Depending on the treatment of the molybdenum nitride catalyst, CO chemisorption on γ -Mo₂N may be modified as shown experimentally.³ Therefore, it is interesting to investigate the adsorption of N/O adatoms on Mo₂N(100) and thereafter CO adsorption on such nitrated or oxinitrided modeling surface. In the following models, the octahedral vacant sites are occupied by nitrogen or oxygen atoms (see Figure 1). On the basis of the reaction



the dissociation enthalpies ΔH_{diss} are calculated to be -2.04 eV/N₂ molecule and -5.32 eV/O₂ one. These results show that an ideal Mo₂N(100) surface is highly active for N₂ and O₂ dissociation from a thermodynamic point of view.¹⁷

What are the effects of such chemically modified surfaces on the CO bonding? When all octahedral vacant sites on the (100) surface are occupied by nitrogen atoms, the corresponding CO + N_{surf} coupling reaction is now exothermic with an adsorption enthalpy of -0.76 eV. The NCO unit is linear with N-C and C-O distances of 1.23 and 1.18 Å, respectively (see Table 1 and Supporting Information for the computed structural information). On the basis of these structural results, one may consider these NCO species as a 16-electron triatomic isocyanate NCO⁻ coordinated to four molybdenum atoms ($d_{\text{Mo}-\text{N}}$ = 2.56 Å). The computed vibrational frequency (2206 cm⁻¹) for the antisymmetric combination of the CO and NC stretching is in good agreement with the experimental assignment of 2200 cm⁻¹; however, this does not take into account the error of 40 cm⁻¹ obtained for the free NCO radical. Another interesting aspect concerning the nitrated surface comes from the decrease of the CO binding energy on the molybdenum sites which are now coordinated to five nitrogen atoms for Mo(1) and four N_{surf} atoms for Mo(2) (see Table 1 and Figure 2). The calculated adsorption energy of -0.60 eV for Mo(1) is close to the one obtained for a hypothetical cubic MoN(100) surface (ΔH_{ads} = -0.67 eV). These results show as expected that the CO binding energy depends highly on the degree of the local coordination of the surface Mo atoms. The calculated vibrational frequencies are 1997 and 1993 cm⁻¹ for Mo(1) and Mo(2), respectively, close to the values obtained for the clean γ -Mo₂N (100). Unexpectedly the stretching frequency of CO adsorbed on-top molybdenum is only slightly modified by the number of nitrogen atoms coordinating the molybdenum atom. The Mo environment does affect more the CO binding energies than the vibrational frequencies. From these results, one may conclude that a freshly nitrated Mo₂N/Al₂O₃ catalyst³ presents Mo surface atoms surrounded by nitrogen atoms and that the IR techniques employed in ref 3 for example could not conclude on the local coordination of the metallic atoms, i.e., the existence of coordinatively unsaturated metallic sites. What about the oxygen effect? Yang and Xin et al.³ show that the surface of a reduced passivated Mo₂N catalyst is in a highly oxidic form, leading to an increase of the on-top CO IR band values up to 2190 cm⁻¹. A hypothetical oxinitride surface is modeled by filling the vacant octahedral site by an oxygen atom, leading to the Mo₂N(100)-O surface: from Table 1, one may see that the calculated vibrational

frequency for CO on Mo(1) increases from 1997 cm⁻¹ on Mo₂N(100)-N to 2034 cm⁻¹ on Mo₂N(100)-O while the adsorption enthalpy decreases by 0.3 eV ($\Delta H_{\text{ads}} = -0.33$ eV for Mo(1)). Going further in the oxygen coverage on the (100) surface leads to the occupation of both octahedral sites (Mo/O = 1, named Mo₂N(100)-2O surface). The interaction of CO with Mo(1) sites coordinated to four oxygen adatoms is slightly attractive by 0.15 eV with an equilibrium Mo-C distance of 2.23 Å. The corresponding CO frequency is computed now to be 2041 cm⁻¹. Changing the local environment of the molybdenum atoms by modifying the nature of the neighboring atoms, in a chemical sense passivating the surface, produces a shift in the ν_{CO} values of only ca. 37–44 cm⁻¹. The corresponding scaled frequencies should be around 2100 cm⁻¹. Such IR bands at 2100 cm⁻¹ have been assigned to CO on Mo³⁺ or Mo³⁺(CO)₂.³ Our calculations for the given models show that they may be assigned to CO molecules coordinated to Mo surrounded by oxygen/nitrogen atoms. The last assignment, Mo³⁺(CO)₂, is not supported by our results since two CO molecules coordinated to Mo are not found due to steric repulsions. From this preliminary study of the passivation effect on CO adsorption, we suggest that the IR bands found in the range of 2150–2200 cm⁻¹ for the reduced passivated Mo₂N/Al₂O₃ catalyst may correspond to adsorbed or physisorbed CO species on oxide surface layers such as that of MoO₂ as mentioned previously by several authors.^{2j,3} Finally, one may conclude that the fully nitrogen-covered surface mimicking the nitrated surface catalyst allows for the formation of NCO species by creating active nitrogen surface sites that can react with carbon monoxide.

Co(g) + N_{surf} Reaction Mechanism

The next step was to study the reaction mechanism between CO and N_{surf} to NCO. The reaction may occur between gas-phase CO and chemisorbed N atoms (the so-called Eley–Rideal mechanism, E–R) or might proceed via the Langmuir–Hinshelwood (L–H) mechanism, which means that the reaction takes place between chemisorbed reactants.¹⁸ As the Mo₂N(100) surface binds the CO molecules so strongly to Mo atoms, the reaction via an L–H process might be disfavored. Furthermore, the experimental FT-IR results show that the intensity corresponding to the linear CO coordination on Mo atoms does not change at all when the reaction occurs.³ Nevertheless, a search for a μ_2 -CO (bridged Mo–CO–N_{surf}) type coordination has been done, but no activated nor intermediate complexes have been located along several pathways. Therefore, we focus our investigation on the E–R mechanism. To do this, we evaluated an appropriate cut through the high-dimensional potential energy surface (PES); this cut is defined by the vertical position of the C atom (z_{C}) and the vertical position of the N_{surf} atom (z_{N}) below the CO molecule. At each point in the PES, the positions of all the atoms were relaxed except the bottom two layers and the positions of the C and N_{surf} which are fixed. The resulting PES is presented in Figure 3, with $z_{\text{N}} = 0$ and $\Delta E = 0$ values relative to the Mo₂N(100)-N + free CO system. A reaction pathway for NCO formation via the E–R mechanism could be identified: when the CO molecule approaches the surface up to $d_{\text{N-C}} > 1.9$ Å, a repulsive interaction occurs, as expected between the CO lone pair and the negatively charged nitrogen adatom. An upward movement of the N_{surf} atom by 0.2 Å toward the CO molecule is calculated at the transition state (marked by an crossed circle): the associated energy barrier is about 1.5 eV with N–C and C–O bond lengths of 1.93 and 1.16 Å, respectively. This activated linear NCO species then moves away from the surface reaching a local minimum with an energy

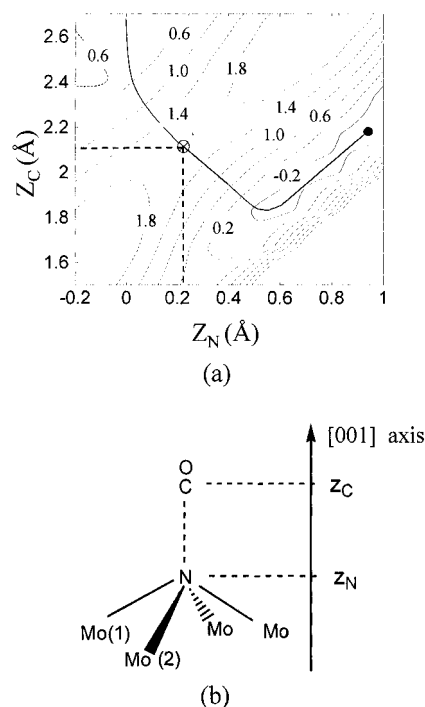


Figure 3. (a) Potential energy surface (PES) for the CO + N_{surf} coupling reaction as a function of the positions of the carbon atom, z_{C} , and of the nitrogen surface atom, z_{N} . The contour-line spacing is 0.4 eV. The crossed circle and full one symbols indicate the calculated transition state and the local minima at -0.76 eV (see text). The zero of energy and of atomic z_{N} position refers to the situation where CO is far away from the Mo₂N(100)-1 \times 1-N surface. A possible reaction pathway is indicated as a guide-eye. (b) Local coordination mode of N_{surf} + CO on the surface: the molecular axes are constrained to be perpendicular to the surface.

gain of 0.76 eV. During this stabilizing process, the Mo–(μ_4 -N) distances increase from 2.22 Å in Mo₂N(100)-N to 2.56 Å in Mo₂N(100)-N/CO due to a charge transfer from the metallic surface to the newly created nitrogen–carbon bond. Note that on releasing the constraint that the CO axis be held perpendicular to the surface, the NCO species remains linear. The tetracoordinated NCO species on molybdenum nitrides may be seen as adsorbed NCO⁻ molecules, isoelectronic to carbon dioxide.¹⁹ A further comment will concern the desorption of surface NCO leading to the open-shell triatomic species. As NCO species are strongly bound to the surface ($\Delta H_{\text{ads}} = +3.40$ eV), it will be difficult to observe it by experimental techniques in the gas phase and furthermore this open-shell triatomic system may react with other gaseous molecules (e.g. H₂).

Summary

Our DFT results may be summarized by looking at the reaction $1/2\text{N}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NCO}(\text{g})$ on a clean γ -Mo₂N(100)-1 \times 1 surface. Figure 4 shows the energetic profile for this gas-phase reaction. (i) N₂ dissociation on the 100 Mo₂N(1 \times 1) surface is thermodynamically favorable by 2.04 eV/N₂ molecule showing the instability of such ideal (stoichiometric) surface. The surface 4-fold vacant sites are highly active vis-à-vis molecular dissociation for O₂ and N₂. The next point will be the theoretical study of possible mechanisms to generate such active sites on nitrated/passivated surfaces, i.e., by hydrogenation of nitrogen or oxygen atoms. (ii) Adsorption of CO on a nitrogen adatom is favorable when the surface is nitrated, leading to the formation of a stable adsorbed NCO species. The calculated

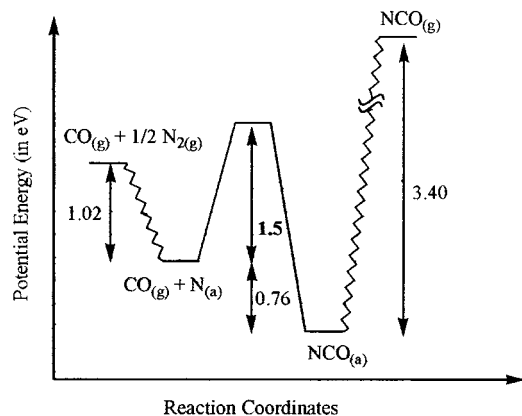


Figure 4. Schematic energy profile for the reaction $1/2\text{N}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NCO}(\text{g})$ at $\text{Mo}_2\text{N}(100)$. Energies are in eV. The zigzag lines indicate that the mechanism pathway has not been studied.¹⁷

vibrational frequencies support the experimental assignments of Yang and Xin et al.³ (iii) The CO adsorption on nitrogen atom proceeds through an Eley–Rideal mechanism with an activation energy of 1.5 eV.

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Supporting Information Available: Figures of geometrical structures with energies for all surfaces discussed in the text and tables of binding energies and geometrical parameters for molecular N_2 , O_2 , CO , and NCO species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(9) Note that carbon monoxide molecules absorb dissociatively on Mo surfaces.

(10) MoN compound crystallizes with a hexagonal structure. See: Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984.

(11) INTDER 95 is a general program developed by Wesley D. Allen and co-workers which performs various vibrational analyses and higher-order nonlinear transformations among force field representations. See: (a) Allen, W. D.; Császár, A. G. *J. Chem. Phys.* **1993**, *98*, 2983. (b) Allen, W. D.; Császár, A. G.; Szalay, V.; Mills, I. M. *Mol. Phys.* **1996**, *89*, 1213. (c) Allen, W. D.; Császár, A. G.; Horner, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 6834.

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(14) (a) Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222. (b) Note that a more pronounced bond length alternation is found in these systems than in the reconstructed $\gamma\text{-Mo}_2\text{N}(100)$ surface.

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(16) Eichler, A.; Hafner, J. *Phys. Rev. B* **1998**, *57*, 10110.

(17) A 2×2 $\text{Mo}_2\text{N}(100)$ slab has been chosen to model the molybdenum nitride surface during the search of the $\text{N}_2(\text{g}) \rightarrow 2\text{N}_{\text{ads}}$ mechanism reaction. Frapper, G.; et al. Work in progress.

(18) See ref 15, p 63.

(19) A similar activation energy has been computed for the $\text{CO} + \text{O}_{\text{surf}}$ coupling reaction on the $\text{Ru}(0001)$ surface. See: (a) Stampfl, C.; Scheffler, M. *Phys. Rev. Lett.* **1997**, *78*, 1500. (b) Bonn, M.; Funl, S.; Hess, Ch.; Denzler, D. N.; Stampfl, C.; Scheffler, M.; Wolf, M.; Ertl, G. *Science* **1999**, *285*, 1042.