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Dimethylamine formation from N-nitrosodimethylamine adsorbed on the Ni{1 1 1} surface from first principles

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ABSTRACT

N-nitrosodimethylamine (NDMA) reaction with coadsorbed hydrogen on the Ni{1 1 1} surface has been investigated in the low coverage regime using first-principles calculations. The results of previous calculations found that isolated NDMA adsorbs on the Ni surface in two different competitive ways as the two most stable configurations. In the *upright* configuration the adsorption is via the ON end. This configuration is slightly preferred energetically to the *flat* configuration, in which the interaction is via the ONN plane. However, this last configuration leads to a facile dissociation of the NDMA molecule via the N—N bond. In the present article, it is found that the formation of dimethylamine (DMA) and NO on the surface is preferred to the formation of other products on the surface from the *flat* configuration in the low NDMA coverage regime. Hydrogen is needed for the DMA formation. Besides that, high coverage of adsorbed hydrogen decreases the activation energy needed to break the N—N bond in the *flat* adsorption configuration.

1. Introduction

Many of the N-nitrosamine compounds attracted attention because of their carcinogenic power and other effects such as diabetes and foetal malformations. Since 1930 it has been reported that N-nitrosamines induce cancer to several small mammals and fish [1–3]. Although no direct link between human cancer and the exposure to N-nitrosamines has been established, it is suspected that this is the case [4].

It is well known that the formation of NDMA occurs in the process of water purification [5–12]. Traditional water treatment techniques (biodegradation, air stripping and activated carbon adsorption) are inefficient methods to degrade NDMA [13,14]. Two experimental techniques seem to be promising treatments for NDMA elimination from drinking water and waste-water: hydrogen-based membrane biofilm reactor (MBfR) [15] and catalysis [14,16–19]. The theoretical efforts of the present article are focused on this last method.

Experimental works have reported NDMA degradation on different metal catalysts (in the presence of hydrogen or in its absence) [14,16–19]. Most of the results show nickel as key element in the catalysts. Nickel seems to be a very active component in the catalysis process even in very small concentrations. Different mechanisms have been proposed for NDMA ($ONN(CH_3)_2$) decomposition under different conditions on metal catalysts [14,16–19]. Two mechanisms for NDMA decomposition on metal surfaces were described in a previous article [20] and they are summarized here:

1. initial N—O bond cleavage of the adsorbed NDMA molecule

   $$ONN(CH_3)_2^{ad} \rightarrow O^{ad} + NN(CH_3)_2^{ad} \tag{1}$$

   to form ammonia (NH_3) and dimethylamine ($HN(CH_3)_2$, DMA), after interaction with hydrogen in several steps.
2. initial N—N bond cleavage of the adsorbed NDMA molecule

   $$ONN(CH_3)_2^{ad} \rightarrow ON^{ad} + N(CH_3)_2^{ad} \tag{2}$$

   to form dimethylamine ($HN(CH_3)_2$) and ammonia (NH_3) or dinitrogen (N_2), after interaction with hydrogen.

Two stable adsorption configurations were reported as the most stable for NDMA on the Ni{1 1 1} surface: *upright* and *flat* [20]. In the *upright* configuration the NDMA molecule is bound to the surface via the ON end to two different atoms of the surface. NDMA dissociation from this configuration is described by Eq. (1). On the other hand, in the *flat* adsorption configuration the NDMA molecule is bound to the surface via the ONN plane to three different nickel atoms. NDMA dissociation from this adsorption configuration is

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described by Eq. (2). It was also shown, in that article [20], that breaking the N—O (Eq. 1) or N—N (Eq. 2) bonds are favorable processes on the Ni{1 1 1} surface. However, the activation energy needed to cleave the N—N bond (Eq. 2) is lower by 0.33 eV than that one needed to break the N—O bond (Eq. 1). This indicates that NDMA fragmentation via the N—N bond cleavage (Eq. 2) seems to be more likely.

In this article, the coadsorption of NDMA adsorbed in the *flat* configuration with low hydrogen coverage on the Ni{1 1 1} surface and the final formation of fragments on the surface are investigated. Low coverage of NDMA is assumed. In this configuration the adsorption takes three metal atoms of the surface. Otherwise, at a higher coverage the *upright* configuration will probably dominate the adsorption. Several adsorption *hollow* sites are studied for H near adsorbed NDMA. Only the hydrogen that adsorbs on the surface is taken into account in this manuscript. The interactions between NDMA and hydrogen described here occur in aqueous environment and the mentioned species could interact not only via the surface but via other mechanisms. Interaction (repulsion) energies are calculated between adsorbates. After that initial interaction two dissociation pathways are investigated:

1. NO and DMA formation

$$\mathrm{ONN(CH_3)_2^{ad} + H^{ad} \rightarrow ON^{ad} + HN(CH_3)_2^{ad}} \qquad (3)$$

2. HNO and $N(CH_3)_2$ formation

$$\mathrm{ONN(CH_3)_2^{ad} + H^{ad} \rightarrow HNO^{ad} + N(CH_3)_2^{ad}} \qquad (4)$$

The results presented here show that although both interaction pathways (Eqs. (3) and (4)) are favorable energetically, NO and DMA formation is more likely to occur (Eq. (3)) from the *flat* configuration at low NDMA coverage. The effect of coadsorbed hydrogen on the energy barrier for NDMA dissociation is also investigated.

2. Methodology

First-principles total energy calculations were performed using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) [21,22]. The Kohn–Sham equations were solved using the projector augmented wave (PAW) approach for describing electronic core states [23,24] and a plane-wave basis set including plane waves up to 400 eV. Electron exchange and correlation energies were calculated within the generalized gradient approximation (GGA) in the Perdew–Wang 91 form [25]. Spin-polarization calculations have been performed for isolated adsorbed and coadsorbed NDMA molecule. Atomic relaxations are considered converged when the forces on the ions are less than 0.03 eV/Å. The climbing image nudged elastic band method (CI-NEB) was used to calculate the activation energies. Only one image was used that was forced to the maximum in the potential energy path between the initial and final stable configurations. In a previous article [20] the CI-NEB method was used to calculate the minimum energy path (MEP) of the isolated adsorbed NDMA molecule using five images. Only one maximum was found and the activation energy for fragmentation was calculated (0.23 eV). In the present report only one image is used in order to calculate or estimate only the activation energy for NDMA fragmentation.

The system (the Ni{1 1 1} surface and the adsorbate(s)) was modeled by a hexagonal supercell with lattice constants $a = 7.471$ and $c = 20.334$Å [26]. The surface was modeled by 4-layer thick slab separated by more than 15 Å vacuum region to avoid interactions between slabs due to periodic boundary conditions. A (3 × 3) surface was used to minimize lateral interactions. The atoms of the two external layers and the adsorbate were allowed to freely relax according to the calculated forces on them. The first Brillouin zone of the supercell was sampled with a $(4 \times 4 \times 1)$ Γ centered mesh, that gives 10 automatic **k**-points. This is the only difference in the computational configuration with respect to the previous report [20].

The adsorption energy, E, was calculated as:

$$E = \mathrm{TE}\left(\frac{\text{adsorbate}}{\text{srf}}\right) - \sum_j \mathrm{TE}_j(\text{adsorbate}) - \mathrm{TE(srf)}$$

the *adsorbate* refers to the adsorbed species. The first term is the energy of the optimized configuration of adsorbed species on the clean relaxed surface. The second term is the gas phase energy of the adsorbate, half of the molecular H_2 energy is used for atomic hydrogen. The third term is the energy of the clean optimized Ni surface. With this definition, negative values of E stand for stable configurations.

3. Results and discussion

In a previous article [20], two stable adsorption configurations were found as the most stable for NDMA on the Ni{1 1 1} surface: *upright* and *flat*. The NDMA molecule binds via the ON end to two nickel atoms of the surface in the *upright* configuration, as shown in the left panel of Fig. 1. In the *flat* configuration, the NDMA molecule binds to three atoms of the surface via its ONN plane, as shown in the central and right panels of Fig. 1. In that article [20] and in the present manuscript, van der Waals (vdW) interactions are not included. If they were included, probably the interactions between the NDMA molecule and the nickel surface would be a bit stronger, mainly in the *flat* adsorption configuration. This means that the calculated adsorption energy would be a bit higher in absolute value. However, the adsorption would not change, probably [27]. The adsorption would still be via the oxygen and nitrogen atoms to three nickel atoms of the surface. The ONN plane would still be nearly parallel to the surface plane, although probably at a different distance [28]. The adsorption of a larger molecule, but still planar, has been studied with and without vdW interactions on the Ag{1 1 1} surface [28]. The calculated adsorption energy of azobenzene is 0.1 eV using PBE but 0.98 eV using vdW-DF [28]. This last value is in agreement with the experimental desorption energy, 1.0 ± 0.1 eV [29]. For NDMA adsorption on the Ni{1 1 1} surface in the *flat* configuration is not expected such a large value for the vdW forces. In fact, on the same surface used in the present manuscript, Ni{1 1 1}, the vdW interactions seem not to be present when adsorption of phenol is investigated using PBE ([30] and references within [31]).

In that article [20], the activation energy needed to dissociate the NDMA molecule into two fragments was calculated. From the *upright* configuration the cleavage of the O—N bond leaves O and $NN(CH_3)_2$ adsorbed on the surface (Eq. (1)). The cleavage of the N—N bond from the *flat* configuration produces NO and $N(CH_3)_2$ adsorbed on the surface (Eq. (2)). The *upright* adsorption configuration is favorable to the *flat* configuration by 0.13 eV. However, the activation barrier to dissociate NDMA from the *flat* configuration into NO and $N(CH_3)_2$ is lower by 0.33 eV. Although the NDMA adsorption in the *flat* configuration is less likely than the adsorption in the *upright* configuration, the NDMA dissociation from the *flat* configuration is much more likely. In order for the NDMA molecule to adsorb in the *flat* configuration low coverage is required, otherwise, the *upright* configuration is going to dominate. In the present report, the coadsorption of H and NDMA in the *flat* configuration, the N—N bond fragmentation and the formation of products are investigated.

Calculated adsorption energy for NDMA in the *flat* configuration is −0.82 eV. The ON, NN, NC and CH calculated bond lengths