Regular Article

Effect of Molecule Coverage on Nitric Oxide Reduction Reaction on Cu(111)

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Abstract

Electrochemical nitrogen oxide reduction reaction (NORR) can simultaneously remove atmospheric pollutant NO and produce the important chemical ammonia (NH_3), which, therefore, has garnered significant attention. However, the effect of molecule coverage on the catalyst surface on electrocatalytic activity is less discussed. In combination with atomic *ab initio* thermodynamics and first-principles calculations, the relationship between the NO coverage and catalytic NORR activity on Cu(111) is unraveled in this work. Results indicate that the adsorption stability and the limiting potential (U_L) of NORR on Cu(111) is closely related to NO coverage. In the case of standard conditions (1 atm, 300 K), NO adsorption with a coverage of 1/4 monolayer (ML) is the most stable configuration, though the corresponding U_L (0.34 V) is higher than those of 1/9 (0.29 V) and 1/16 ML (0.29 V) adsorption while significantly lower than that of 1 ML (0.78 V). Therefore, our study provides insights into the role of temperature, pressure, and molecule coverage in electrochemical reactions.

Key words: NORR, Cu(111), molecule coverage, first-principles calculations.

1. Introduction

Nitric oxide (NO) is a major atmospheric pollutant. Excessive emission of NO contributes to environmental issues including acid rain, photochemical smog, and global warming, all of which not only cause significant disruptions to human life but also pose substantial threats to public health and survival [1–6]. To address this issue, various denitrification methods have been proposed, with selective catalytic reduction (SCR) being the most widely utilized technology. Through SCR, NO can be converted into harmless nitrogen (N_2) gas and released into the atmosphere [7]. However, SCR presents several challenges including high consumption of expensive reactants and excessive energy requirements, making it economically unfeasible and environmentally unsustainable [8–11].

Ammonia (NH_3) is one of the most important chemicals in industry, with widespread applications in the production of explosives, synthetic fibers, fertilizers, and pharmaceuticals. Currently, NH_3 production in industry primarily relies on the Haber–Bosch process, which requires harsh conditions of high temperature and high pressure, accompanied by substantial energy consumption and the release of significant amounts of greenhouse gases [12–15]. In order to overcome these drawbacks, electrochemical N_2 reduction reaction (NRR) has recently garnered intensive interest. NRR occurs under mild conditions and does not generate large amounts of polluting gases, manifesting itself as a promising alternative to the Haber–Bosch technology and attracting significant attention [16,17]. However, NRR faces two significant challenges: (1) low catalytic activity due to the chemical inertness of N_2, and (2) low Faradaic efficiency (FE) because of the "'latex competing hydrogen evolution reaction (HER). Therefore, there is an urgent need to explore sustainable and environmentally friendly alternatives for efficient NH_3 production.

The concept of directly electrochemically reducing NO to simultaneously remove NO and synthesize NH_3 has been put forward [18–20]. This approach has quickly gained extensive attention as NO exhibits higher chemical reactivity than N_2, which endows the NO reduction reaction (NORR) better activity and selectivity compared to NRR. Experimental and theoretical studies have reported various electrocatalysts for NORR, such as Pt(111) [21], defective hexagonal boron nitride [22], as well as a CoN_4 moiety [23]. In particular, Cu(111) was demonstrated to have relatively high catalytic NORR activity and excellent

NH_3 selectivity, by investigating the adsorption free energy of NORR intermediates on different transition metals [18]. It should be emphasized that, for NORR, N–N coupling under high NO concentrations will lead to the formation of byproducts such as N_2O (with a global warming potential 298 times greater than CO_2) and N_2. It was found that, additionally, the generation of single N products (NH_3) on Cu(111) is favored at low NO coverages [24]. It therefore can be concluded that the electrochemical reaction and the catalytic NORR activity on Cu(111) is in close relation with the molecule coverage on the catalyst surface. Unraveling this relationship is of importance for optimizing the activity and selectivity and helps further understanding the NORR mechanism. However, a comprehensive study on the effect of NO coverage on NORR is missing.

In this work, based on the atomic *ab initio* thermodynamics in conjunction with first-principles calculations, we find that the NO molecular coverage on Cu(111) affects the catalytic NORR activity and there is a competition between the stability of the adsorption structure and the NORR limiting potential (U_L). In the case of high coverage of 1 monolayer (ML), intermolecular repulsion inhibits NO activation, resulting in a high energy barrier of 0.78 eV for the potential-determining step (PDS). It is of interest to see that the U_L decreases to 0.34, 0.29, and 0.29 V as the NO coverage decreases to 1/4, 1/9, and 1/16 ML, respectively. It should be emphasized that the adsorption structure with a 1/4 ML NO coverage is the most stable one under standard conditions (1 atm, 300 K), though it does not provide the optimum catalytic NORR activity. In this view, therefore, our results provide new insights into the effect of molecular coverage on the catalytic activity in electrochemical reactions.

2. Calculation Methods

In this work, the first-principles calculations based on spin-polarized density functional theory (DFT) were performed by using the Vienna *ab initio* simulation package (VASP) [25,26]. In order to describe the core–valence interactions, the projector-augmented wave (PAW) method [27] was used with a cutoff energy of 500 eV for the plane-wave basis set. In the framework of the generalized gradient approximation (GGA), the Perdew–Burke–Ernzerhof (PBE) scheme [28–30] was applied for the exchange–correlation functional. The convergence criteria for energy and residual force were set to 10^{-5} eV and 0.01 eV/Å, respectively, and a Monkhorst–Pack k-point mesh of $3 \times 3 \times 1$ was used for structure optimization and total energy calculation. To account for the van der Waals (vdW) interactions between the catalyst and NORR intermediates were described by employing the DFT–D2 scheme [31]. A Cu(111) surface was modeled by a slab, and a vacuum layer of 20 Å along the z direction was added to avoid interactions between periodic images.

In light of the atomic *ab initio* thermodynamics, the surface free energy γ can be employed to determine the stability of a surface in contact with a gas-phase reservoir, which is defined as

$$\gamma(T, \{p_{NO}\}) = \frac{1}{A}\Big[G^{surf} - n_{Cu}\mu_{Cu}^{bulk} - n_{NO}\mu_{NO}^{gas}(T, p_{NO}) \Big],$$

where G^{surf} is the Gibbs free energy of the solid exposing the surface, A is the surface area, and μ_{Cu}^{bulk} and μ_{NO}^{gas} are the chemical potentials of bulk Cu and gaseous NO, respectively. To evaluate the stability of NO adsorption on Cu(111), the Gibbs free energy of

adsorption ΔG^{ads} was calculated, which can be defined as [32,33]

$$\begin{aligned}
\Delta G^{ads}(\Delta\mu_{NO}) =& \gamma_{Cu(111)} - \gamma_{NO/Cu(111)} \\
=& -\frac{1}{A}\Big[G_{NO/Cu(111)}^{surf} - G_{Cu(111)}^{surf} \\
& - \Delta n_{Cu}\mu_{Cu}^{bulk} - n_{NO}\left(E_{NO}^{tot} + \Delta\mu_{NO} \right) \Big] \\
\approx& -\frac{1}{A}\widetilde{E}_{NO/Cu(111)}^{bind} + \frac{n_{NO}}{A}\Delta\mu_{NO}
\end{aligned}$$

where $G_{NO/Cu}^{surf}$ and $G_{Cu(111)}^{surf}$ are the Gibbs free energies of the Cu(111) surface with n_{NO} adsorbed NO molecules and the clean Cu(111) surface, respectively. In particular, the chemical potential of NO is composed of its total energy part and the temperature- and pressure-dependent term, that is,
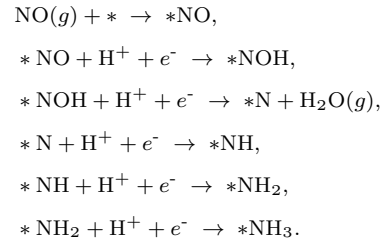
$$\mu_{NO} = E_{NO}^{tot} + \Delta\mu_{NO}(T, p).$$

It has been confirmed that the difference in Gibbs free energies between the clean and the NO-adsorbed surfaces can be obtained from DFT results [34,35].

According to the computational hydrogen electrode (CHE) model proposed by Nørskov *et al.* [36], the Gibbs free energy change for each NORR step is determined by

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S,$$

where ΔE is the reaction energy of each elementary step, ΔE_{ZPE} is the zero-point energy correction, and ΔS is the entropy change at room temperature (298.15 K). In an O-distal reaction pathway, the NORR proceeds stepwise as follows:

$$\begin{aligned}
NO(g) + * &\rightarrow *NO, \\
*NO + H^+ + e^- &\rightarrow *NOH, \\
*NOH + H^+ + e^- &\rightarrow *N + H_2O(g), \\
*N + H^+ + e^- &\rightarrow *NH, \\
*NH + H^+ + e^- &\rightarrow *NH_2, \\
*NH_2 + H^+ + e^- &\rightarrow *NH_3.
\end{aligned}$$

3. Results and discussion

It is well known that the adsorption and activation of NO is both the first and most crucial step in the NORR process, essential for the entire electrocatalytic reaction. In other words, sufficient NO adsorption strength is required, and efficient NO activation facilitates a thermodynamically easier initial protonation step. It has been demonstrated that the NO molecule on Cu(111) prefers to adsorb at the CuCuCu hollow site among the possible NO adsorption sites (Cu site, Cu–Cu bridge site, and CuCuCu hollow site) in a N-end configuration [37]. On Cu(111), further studies have shown that the NORR pathway is confirmed to follow the O-distal pattern, as illustrated in Figure 1a. In this reaction pathway, $H^+ + e^-$ first attacks the distal O atom of NO, resulting in the formation of an H_2O molecule. Subsequently, the coupled $H^+ + e^-$ continues to attack the remaining N atom, eventually producing an NH_3 molecule, which then detaches from the catalyst surface. It is important to note that the generation of byproducts other than NH_3 is a significant challenge for the NORR process. In particular, NO adsorption at high coverage