

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 catalyst surface on electrocatalytic activity is less discussed. In combination of atomic *ab initio* thermodynamics and the 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 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 the 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 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 competing hydrogen evolution reaction (HER). Therefore, there is an urgent need to explore sustainable and environmentally friendly alternatives for efficient NH_3 production.

It should be emphasized that the cleavage energy of N–O bond is considerably lower than that required to dissociate the ultrastable $\text{N}\equiv\text{N}$ triple bond, and thus the N–O bond is more amenable to activation. Therefore, utilizing highly soluble nitrogen oxides, such