A density functional study for adsorption and oxidation of NO on Ir (1 0 0) surface

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ABSTRACT

Density functional theory (DFT) calculations are used to investigate the adsorption of nitrogen oxides (NO$_x$) (x = 1, 2) and oxidation reaction on Ir (1 0 0) surface. On clean surface, NO molecule energetically prefers to bond at bridge sites for all studied coverages (Θ = 0.25, 0.50, 0.75 and 1.00) monolayer (ML). An electron donation from the occupied orbitals to the d metal band and a back donation from the substrate to the 2π^* orbital occur for adsorbed NO on Ir (1 0 0) surface, which causes an increase in N—O bond. NO$_2$ molecule exhibits a variety of adsorption geometries; the most energetically favorable is the μ-N,O-nitrito configuration with an adsorption energy 1.91 eV. The reaction pathway and the transition state (TS) are determined using constrained minimization method. At the TS, the adsorbed oxygen (O$_a$) atom and NO molecule diffuse to less stable states (top). Then they react to form chemisorbed NO$_2$ with activation energy about 1.41 eV.

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1. Introduction

The efforts to reduce nitric oxide pollutants over transition metal surfaces have been large because it is a key process towards controlling the air pollution. Iridium is one of the most promising metals to reduce NO$_x$ to N$_2$ under oxygen rich conditions from lean-burn engines [1–3]. Understanding the chemisorption and heterogeneous catalysis on metal surfaces requires a detailed knowledge of the adsorbate structures and energetics with respect to the substrate [4,5]. The catalytic oxidation of NO to NO$_2$ [1] is also a major topic in this respect [3,6–8], since it has been found that during the lean burn, NO oxidizes to NO$_2$ as follows:

$$NO + (1/2)O_2 \rightarrow NO_2. \tag{1}$$

Afterwards NO$_2$ was found to react with hydrocarbons on the surface of the catalyst [9–12].

Gardner et al. [13] have found that the adsorption of NO on the metastable (1 × 1)–Ir (1 0 0) surface is dissociative at 300 K using vibrational spectroscopy and low-energy electron diffraction (LEED) at low coverage. At 90 K no dissociation happens and NO molecules are adsorbed on top and bridge sites. Their results show that Ir (1 0 0) has low dissociative sticking probability for NO and there is a correlation between the substrate structure and the decomposition of NO. Khatua et al. [14] combined experiment with

DFT calculations to study the adsorption of NO on Ir (1 0 0) as a function of NO coverage and temperature. They reported that for unreconstructed Ir (1 0 0)–(1 × 1) surface exposed to 10 L of NO, the bridge band dominates the spectra up to 287 K due to differences in the dynamic dipole moment for different adsorption sites. At around 319 K the top band becomes stronger, which indicates that NO molecules gain the energy barrier to diffuse from the bridge site to the top site. Due to the small dissociation energy of NO molecule compared with that of CO (630 kJ/mol and 1076 kJ/mol for NO and CO, respectively), Brown and King reported that both molecular and dissociative adsorptions of NO occur on Ir surfaces [15]. Using high resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS), Jiang et al. [16] found that the repulsive interaction between the pre-covered O$_a$ and NO on Pt (1 1 0) surface is stronger on the bridged NO than on the linear one (NO on top site). This is attributed to the geometric positions of pre-covered O$_a$ as well as the bridged and the linear NO on the surface. They found that due to the strong repulsive interactions with pre-covered O$_a$, the bridged (but not the linear) NO, experiences a decrease in the heat of adsorption. Electronegative O$_a$ might locally weaken the ability of Pt to back donate electron density into the 2π^* orbital of NO, which leads to a decrease in the strength of Pt—NO bond. They concluded that the repulsive interactions dominate the influence on NO exerted by the coexistence of O$_a$. Liu et al. [10] combined energetic data from density functional theory with thermodynamic calculations and found that excess O$_2$ can readily poison the Ir catalyst for NO reduction and the poisoning starts at low O coverage on the

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