

Investigation of CO Adsorption on Ni Surface with Regarding the Nearest-Neighbor Interactions between Adsorbates

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Abstract

In this work, we consider thermodynamic properties of $p(\sqrt{7} \times \sqrt{7})R19^\circ$ structure, which appears at the coverage of $\theta = 4/7\text{ML}$ when $T \leq 220\text{ K}$, with regarding the

nearest-neighbor interactions among adsorbates. The structural study of Held et al. [1] shows that at this coverage, the CO molecules bind to on-top (onefold coordinated) and bridge (twofold coordinated) substrate sites with a relative population of 1:3 respectively (Fig 1) [2]. For this coverage, the nearest neighbor interactions are significant and thereby the particles distribution on these sites is not random [3]. Our goal is to include such interactions on the particles distribution.

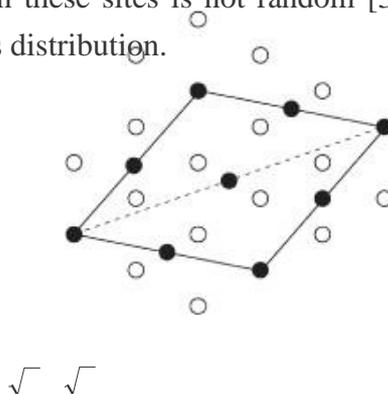


Figure 1. Unit cell of the $p(\sqrt{7} \times \sqrt{7})R19^\circ$ structure proposed by Held et al. (●) denotes CO molecules and (O) the underlying metal atom [2].

Introduction

Carbon monoxide adsorption on the close packed Ni (111) surface belongs

undoubtedly to the most thoroughly investigated adsorption systems. However, there are still unsolved problems concerning the microscopic structure and occupation of surface

sites with varying CO coverage [4-5]. For the Ni(111) structure, there are four kinds of adsorption sites, where their occupation depends on the coverage (Fig 2) [4]. Several low energy electron diffraction (LEED) patterns are reported in the literature: $p(2 \times 2)$ at $\theta = 1/4\text{ML}$, in which fcc and hcp sites are occupied, a faint $p(\sqrt{3} \times \sqrt{3})$ pattern at $1/3\text{ML}$, in which only bridge sites are occupied and finally (for adsorption below 220 K) a $p(\sqrt{7} \times \sqrt{7})R19^\circ$ structure which occurs at the saturation coverage of $\approx 4/7\text{ML}$. At this coverage, on-top and bridge sites are occupied. At 80 K the surface coverage can be increased even up to $5/8\text{ML}$, characterized by a $c(2\sqrt{3} \times 4)$ rect structure, in which Low-symmetry sites are involved [5-6].

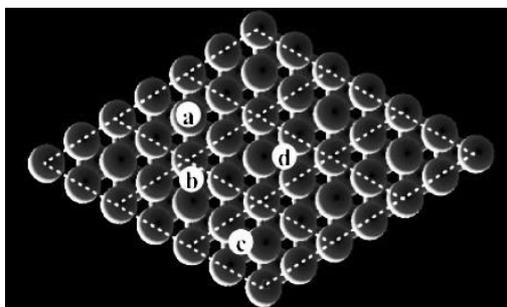


Figure 2. Top view of Ni(111): (a) on-top site, (b) bridge site, (c) hexagonal-close-packed (hcp)site, (d) face- centered cubic (fcc) site [6].

Method:

To consider thermodynamic properties of $p(\sqrt{7} \times \sqrt{7})R19^\circ$ structure, which appears at $\theta = 4/7\text{ML}$ when $T \leq 220\text{ K}$, with regarding of the nearest- neighbor interactions among adsorbates, we have used CVT¹ [7]. The unit cell used as a basic figure must contain all kinds of interactions. To calculate thermodynamic properties of $p(\sqrt{7} \times \sqrt{7})R19^\circ$ structure by CVT, we should first estimate a_n^m , X_n^m and Y_n^m parameters and also the interaction energies, where a_n^m is number of m in a n figure, $X_n^m N$ is number of m figures in the lattice and $Y_n^m N$ is the difference of number of figures in $X_n^m N$ assembly and the lattice. $X_n^m N$ is the number of basic figures in the lattice. DFT calculations have been used to estimate the interaction energies between

¹ Cluster Variation Theory

adsorbates. Then, with minimization of free energy with respect to probabilities, we have estimated the probabilities and then the configurational energy and entropy. Minimization of free energy must be done under appropriate constraints: 1) The normalizing conditions for all figures 2) The constraint for the given coverage. Minimization process is done by MAPLE 9 and MATHEMATICA 10 softwares.

The following expression is used for the configurational free energy:

$$F = \sum_{m=a}^n y_n^m F^m \{P_i^m\}$$

where

$$F^m \{P_i^m\} = N \sum_i \lambda_i^m P_i^m (\epsilon_i^m + kT \ln P_i^m)$$

ϵ_i^m is the summation of adsorption energy and interaction energy for Figure m with i configuration.

Results

The result for the configurational energy is shown in Fig 3. As we expect, with increasing of temperature, configurational energy rises because more energy levels become available for the molecules. For checking the results, the calculated value at the high temperature limit is compared to its exact value, at which the particle distribution is random.

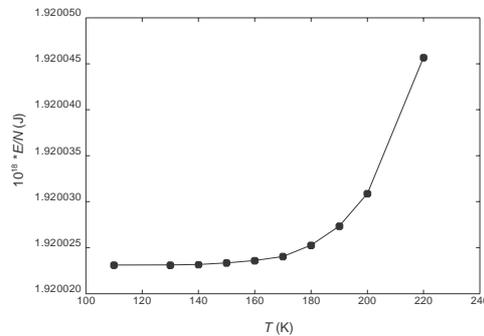


Figure 3. Configurational energy verse temperature for $p(\sqrt{7} \times \sqrt{7})R19.1^\circ$ structure at at $\theta = 4/7ML$ when $T \leq 220$ K.

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