Determination of lateral interactions between NO molecules on Rh(111)

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Abstract. In this study, the STM was used to locally study the adsorption of NO on a Rh(111) single crystal. Three new structures were identified. At 200 K, patches of the (4 × 2)-2NO and an unreported (2 × 2)-2NO structure were found at about 0.50 ML coverage. Higher exposure gave rise to a (2 × 2)-3NO structure with all molecules adsorbed in the hcp sites. At 5 K, a (4 × 4)-1NO structure was observed. The large separation between the molecules can only arise from repulsive interactions over a distance of at least four times the lattice constant (11 Å). Here the interaction is estimated to be of the order of ∼10 K or ∼0.1 kJ/mol. Dynamic Monte Carlo simulations taking into account adsorption, diffusion and pairwise interactions between adsorbates were used to fit the lateral interaction for the next-next nearest neighbor to the patched STM topograph at 200 K for 0.50 ML coverage. The value was determined to be 2 kJ/mol. Using pairwise interactions only, the (2 × 2)-3NO structure could not be explained. It might therefore be necessary to include three-particle interactions. Recent DFT calculations support this idea by showing attractive three-particle interactions.

1. Introduction

The system of NO of rhodium is interesting because of its application in catalytic converters in cars, since rhodium can efficiently transform NO into N2 and O2. To gain more understanding this system has been extensively studied under UHV conditions. At low coverage below 275 K, NO adsorbs molecularly on Rh(111). Two different ordered structures have been found using LEED [1, 2, 3]: at 0.50 ML a zig-zag like (4 × 2)-2NO structure was deduced. In this structure the NO molecules are adsorbed in fcc and hcp sites. At 0.75 ML, a (2 × 2)-3NO structure is reported in which the NO molecules occupy the hcp, fcc and top positions.

The binding strength of molecules adsorbed on a surface can be perturbed by the presence of neighboring species. Not only the nature of the formed structures like the ones discussed above can be influenced but also reaction rates and hence the selectivity of processes. By gaining more insight in adsorbate-adsorbate, or lateral interactions, it might even become feasible to make use of them as they can change reaction routes that would otherwise be unfavorable. In the end, more efficient catalytic processes could be made. The formation of HCN from HCx fragments and N-atoms on Rh(111) at relatively low temperatures is an example [4].

Different techniques can be used to quantify lateral interactions. By calculating the total energy of different coverages using density functional theory (DFT), it is possible to derive some
values of the interactions. The method has the inherent drawback that, as the interactions are small and are obtained by subtracting total energies, the inaccuracy is large. The experimental results obtained from methods like calorimetry and temperature programmed desorption (TPD) have been simulated by monte carlo (MC) calculations in order to obtain the lateral interactions by fitting the simulated curve with the experimental one [5, 6]. In [6], Dynamic Monte Carlo (DMC) simulations on the NO on Rh(111) system showed that the formation of the \((4 \times 2)\)-2NO structure at 0.50 ML strongly depends on the next-next nearest neighbor interaction between the NO adsorbates. Field ion microscopy (FIM) and, later on, scanning tunneling microscopy (STM) were used to directly determine pairwise lateral interactions [7, 8, 9, 10, 11]. Recently it was shown that pairwise interactions are not always sufficient to describe the formed patterns [12, 13] and many-body effects have to be taken into account.

**Figure 1.** A) Topographic STM image \((11 \times 11 \text{ nm}^2)\) showing patches of the \((4 \times 2)\)-2NO (indicated by white zig-zag lines) and \((2 \times 2)\)-2NO structure in a ratio of \(~50\%\). B) Zoom \((1.6 \times 1.1 \text{ nm}^2)\) on the \((2 \times 2)\)-2NO structure showing the individual molecules.

**Figure 2.** A) Topographic STM image \((11 \times 11 \text{ nm}^2)\) showing the transformation of the \((2 \times 2)\)-2NO into the \((2 \times 2)\)-3NO structure. B) Zoom \((1.4 \times 1.7 \text{ nm}^2)\) on the \((2 \times 2)\)-3NO structure showing the individual molecules.

The focus of this paper is on the observation of structures of NO adsorbed on a Rh(111) single crystal in real space by a local probe (STM). In an attempt to quantify lateral interactions, the DMC simulation method of [6] was used. As far as we know the only STM experiment on this system was performed in a different regime (in equilibrium with the NO gas phase in the torr pressure range at room temperature) [14]. It was shown that different patches of the \((2 \times 2)\)-3NO and \((3 \times 3)\)-7NO structure coexisted.

2. Experiment

The STM instrument used in this experiment is a commercially available low temperature STM (Omicron GmbH). Deposition of NO gas can be done in situ. The Rh(111) surface was cleaned by repeated cycles of sputtering (beam energy: 1.5 keV, sample current: 1.5 \(\mu\)A for 90 minutes) at 600°C and annealing at 600°C, 700°C and 800°C (20 minutes for each temperature). At the end of each cycle, the sample was flashed to 1200°C. The NO deposition was carried out at 200 K and 5 K.

Adsorption of \(~1 \text{L} (=10^{-6} \text{torr-s})\) of NO at 200 K gives rise to a \(~0.5 \text{ML} \)coverage with patches of the known zig-zag \((4 \times 2)\)-2NO and an unreported \((2 \times 2)\)-2NO in a ratio of about
50% as is depicted in Fig. 1A. In both structures, the NO molecules are adsorbed in the hcp and fcc sites. A zoom on the (2 × 2)-2NO structure in the inset of the figure (Fig. 1B) shows arrangement of the individual NO molecules. The bright spots filling the honeycomb structure of the (2 × 2)-2NO patches are NO molecules in top sites. Between two consecutive scans (± 30 s), however, these molecules had already hopped to other sites, indicating the weak strength of the NO-top bond.

At a higher dose, the surface structure was converted from the patched adlayer of Fig. 1A to a 0.75 ML (2 × 2)-3NO structure. This structure has all molecules adsorbed in hcp sites and is shown in the inset of Fig. 2. This is different from the previous reported (2 × 2)-3NO structure in which the molecules occupied the hcp, fcc and top sites. Fig. 2A is an intermediate scans in the transition from Fig. 1 to a fully covered (2 × 2)-3NO structure. It shows that the structure started out from the (2 × 2)-2NO patches. A possible explanation could be the loosely bound top NO that moves from the top position to a hcp site, forcing the whole structure to change to a denser (2 × 2)-3NO structure that later on expanded into the (4 × 2)-2NO structure.

Finally, an additional experiment has been conducted to look at the structures formed when adsorbing at 5 K. The sample was inserted in the STM stage in a cold (5 K) and dilute (∼ 2 · 10⁻¹⁰ mbar) NO gas background. The formed (4 × 4)-1NO structure that emerged is depicted in Fig. 3.

**Figure 3.** STM image (50 × 45 nm²) showing a (4 × 4)-1NO structure formed at adsorption at 5 K.

**Figure 4.** Lateral interactions for the Dynamic Monte Carlo model taking into account pairwise interactions up to the next-nearest neighbor.

3. Dynamic Monte Carlo simulations

As was explained in [6], the formation of either the (4 × 2)-2NO or the (2 × 2)-2NO structure strongly depends on the repulsion between the adsorbate and its next-next nearest neighbor. Based on DFT calculations the nearest neighbor sites are excluded for adsorption because of the large repulsion at close distance. The next nearest neighbor was calculated to have a repulsive interaction of 26 kJ/mol (see Fig. 4). The next-next nearest neighbor interaction, however, is in the error margin of the calculation meaning that it could have any value between 0 and 5 kJ/mol. By making use of the DMC model of [6], we tried to fit the calculation to the experimental picture (Fig. 1) by tuning this parameter, and thereby obtain a quantitative value for the next-next nearest neighbor interaction. In Fig. 5, three different simulation results are
depicted. The first simulation was performed with a next-next nearest neighbor interaction of 0 kJ/mol, resulting in grains of the $(2 \times 2)$-2NO structure only. The second picture shows the simulation with an interaction of 5 kJ/mol, giving rise to grains of the $(4 \times 2)$-2NO structure only. By going to an intermediate value of 2 kJ/mol, a mix of both the $(2 \times 2)$-2NO and $(4 \times 2)$-2NO were observed, as shown in the last picture. The above can be understood by looking at the amount of next-next nearest neighbors that an adsorbate has in either of the structures. In both cases, the next-next nearest neighbor also is the closest neighbor. The $(2 \times 2)$-2NO structure has three next-next nearest neighbors whereas the $(4 \times 2)$-2NO has only two. So as soon as the repulsive interaction is significantly larger than the temperature, the adsorbates accommodate to have as few next-next nearest neighbors as possible. In that case, the $(4 \times 2)$-2NO structure is preferred over the $(2 \times 2)$-2NO structure. Expressed in a temperature, the fitted value of 2 kJ/mol is about 240 K and at an adsorption temperature of 200 K, an adlayer consisting of a mix of both structure can therefore be expected.

Figure 5. Results of the Dynamic Monte Carlo Simulations. Dark blue dots indicate molecules that occupy a hcp site, light blue dots are molecules on a fcc site and red dots are molecules on a top site. To guide the eye, circles are drawn in case of the $(2 \times 2)$-2NO honeycomb structure and zig-zag lines to indicate the $(4 \times 2)$-2NO structure.

In the structure that forms at 5 K (Fig. 3), as opposed to 200 K, the temperature is far too low for diffusion to occur. So the formation of the structure is governed by adsorption only. Once one molecule adsorbs, the other cold molecules in the gas do not have enough (kinetic) energy to overcome the lateral repulsion over a distance of four times the lattice constant $(4 \times 2.69 \text{ Å} = 10.8 \text{ Å})$. So the lateral repulsion at 11 Å can be estimated to be of the order of 10 K or 0.1 kJ/mol. This way lateral interactions could in principle be determined as a function of distance by varying the temperature.

Just as for the $(2 \times 2)$-2NO structure, DMC calculations have been performed to reproduce the high density $(2 \times 2)$-3NO structure. However, so far, this structure could not be obtained using pairwise interactions only. In order to explain the $(2 \times 2)$-3NO structure, three-particle interactions might have to be taken into account. Recent DFT calculations indicate that all interactions are repulsive except for an attractive three-particle interaction in which the adsorbates are grouped in a triangle of nearest hcp sites. As the unit cell of the $(2 \times 2)$-3NO structure consists of these kind of triangles, this is a strong indication that it is important to include three-particle interactions in order to model the system correctly. However, the DMC simulations including the three particle interactions still have to be performed.
4. Conclusion

The adsorption of NO on Rh(111) was studied by STM and modeled by Dynamic Monte Carlo simulations. A next-next nearest neighbor interaction between the adsorbates was determined to be 2 kJ/mol by matching DMC simulations to the experimental observation of a patched adlayer of a (4 × 2)-2NO and a unreported (2 × 2)-2NO structure. A new (2 × 2)-3NO structure in which all NO molecules are adsorbed in hcp sites, emerged from the (2 × 2)-2NO patch as the exposure was increased. This structure could not be reproduced in the DMC simulations using pairwise interactions only. However, there are strong indications that three particle interactions have to be taken into account in order to obtain this structure. Furthermore it is shown that lateral interactions as a function of distance could in principle be determined in this way by varying the adsorption temperature. As an example the lateral interaction at a distance of 11 Å is estimated from a (4 × 4) structure to be of the order of 0.1 kJ/mol by adsorbing NO at 5 K.

5. References

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