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Selectivity changes due to restructuring of the Pt(533) surface in the $NH_3 + O_2$ reaction

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Ammonia oxidation with oxygen over Pt(533) in the pressure range 10^{-7}–10^{-3} mbar has been studied using LEED and scanning tunneling microscopy (STM) to detect reaction-induced structural changes. Below 620 K, strong hysteresis effects in the rate occur upon cyclic variation of one of the p, T parameters. The rate changes are associated with structural modifications of the substrate. The Pt(533) surface exhibiting single atomic steps after preparation undergoes a doubling in step height and terrace width connected with a shift in selectivity from preferential N_2 production to strong NO formation. Restoring the single atomic steps in vacuum requires heating above 1100 K, but under reaction conditions the substrate changes are reversible at least down to 600 K.

KEY WORDS: stepped Pt surface; ammonia oxidation; scanning tunneling microscopy; catalyst restructuring; hysteresis effects.

1. Introduction

Catalytic reactions are known to modify the surface of a catalyst often associated with an activation or deactivation process [1–5]. These modifications may lead to real morphological changes. A well-known example is the so-called Ostwald process in which NO is produced by passing ammonia with oxygen at $T \approx 800$–$1000\,^{\circ}\mathrm{C}$ over a Pt/Rh gauze [6]. A number of phenomenologically oriented studies have been carried out by the group of Schmidt [1–4], but not much is known about the microscopic mechanism behind these morphological changes. Here, we use LEED (low-energy electron diffraction) and STM (scanning tunneling microscopy) to study reaction-induced structural changes on a stepped Pt(111) surface, which we expose to $NH_3 + O_2$ at varying temperatures.

NH_3 reacts with O_2 to form mainly N_2 and N_2O at low temperature and NO at high temperature ($T > 800$ K) [6]. The main competing channels are:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

A mechanistic scheme has been proposed by Fogel *et al.* [7]. Pignet and Schmidt studied the kinetics of ammonia oxidation over Pt wires in the 0.1–1 mbar range [3]. At low pressure ($p < 10^{-3}$ mbar) no N_2O has been detected with Pt catalysts. Single-crystal studies of $Pt/NH_3 + O_2$ have been conducted with Pt(100) by the group of King using molecular beam methods and vibrational spectroscopy [8,9], with Pt(111) employing molecular beams in combination with laser-induced fluorescence [10,11], with vibrational spectroscopy [12], and with Pt(s)-12(111) × (111) using mass spectrometry and Auger electron spectroscopy [13].

2. Experimental

The reaction has been studied here in a standard UHV system equipped with LEED, a retarding field analyzer for Auger electron spectroscopy, a scanning tunneling microscope (DME), and a differentially pumped quadrupole mass spectrometer for rate measurements. All STM images shown here were taken near 300 K. The Pt(533) sample was prepared by repeated cycles of Ar ion sputtering ($E = 1$ kV, $p_{Ar} = 2 \times 10^{-5}$ mbar, $t = 15$ min), oxygen treatments ($p_{O_2} = 1 \times 10^{-6}$ mbar), and annealing to $T = 1300$ K. The Pt(533) surface which in a different notation can be written as $4(111) \times (100)$ consists of four (111) terrace units followed by a monoatomic (100) step as demonstrated by the ball model in figure 1(a). The STM image of the clean surface shown in figure 1(b) and the LEED pattern in figure 1(c) showing split integral order beams corroborate the anticipated structure.

3. Results and discussion

The kinetics of N_2 and NO production were studied in the pressure range 10^{-7}–10^{-3} mbar starting always with the structurally well-defined clean surface one obtains after annealing to 1300 K. Figure 2 displays the kinetics of NO and N_2 formation for fixed $p_{NH_3} = 1 \times 10^{-4}$ mbar as p_{O_2} is slowly varied cyclewise at two different temperatures. Upon increasing p_{O_2}, starting from the freshly prepared surface, both N_2 and NO formation increase

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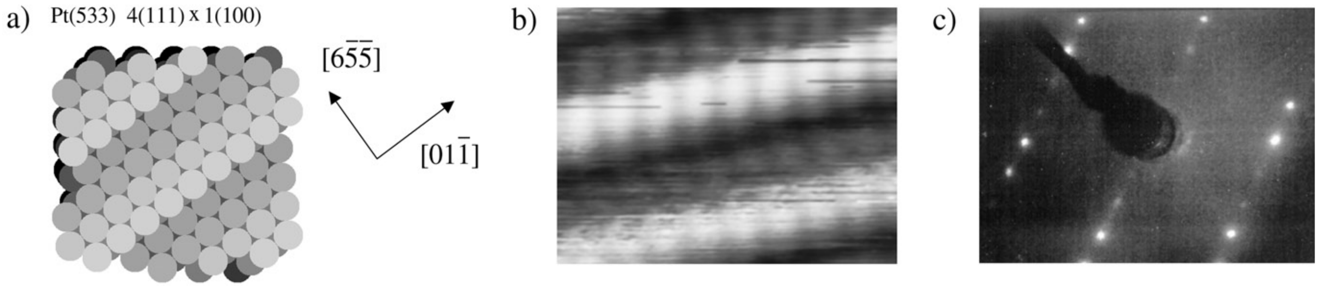

Figure 1. Structural model of the Pt(533) surface (a) and characterization by STM (b) and LEED (c). The STM image (16 × 23 Å^2) was recorded at 300 K with a tunneling voltage $U_t = 20$ mV and $I_t = 1$ nA. The LEED pattern was taken at $E = 88$ eV.

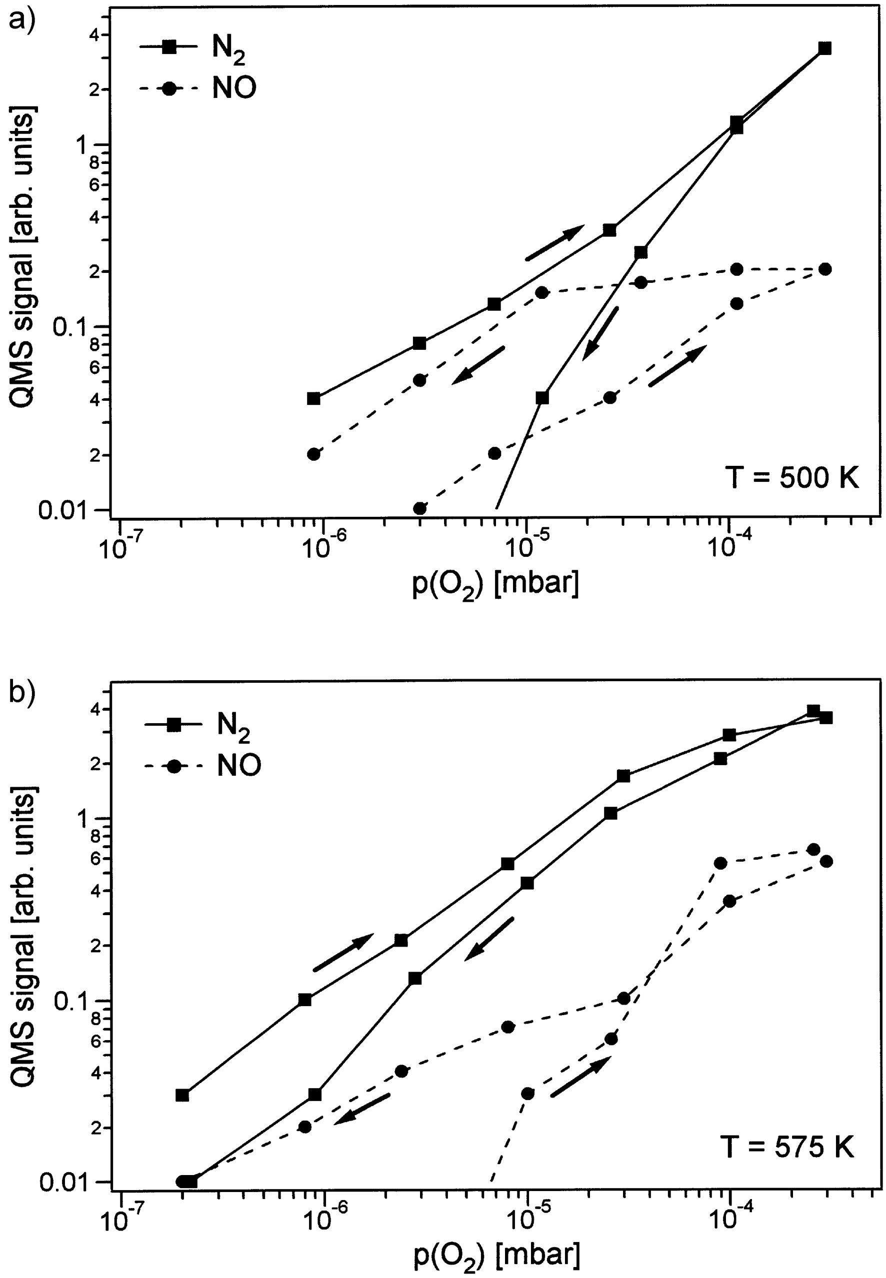

Figure 2. Hystereses in the kinetics of N_2 and NO formation at $T = 500$ K (a) and $T = 575$ K (b) for fixed $p_{NH_3} = 1 \times 10^{-4}$ mbar, and p_{O_2} being varied cycle-wise. The starting point of a p_{O_2} cycle was a freshly prepared Pt(533) surface. The waiting period at each data point was roughly 2 min.

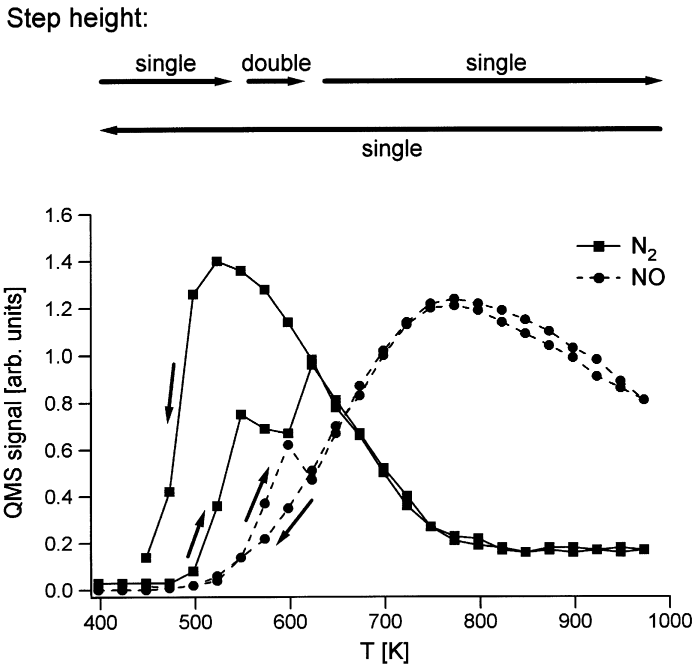

Figure 3. Temperature dependence of NO and N_2 formation for fixed $p_{NH_3} = 1 \times 10^{-5}$ mbar and $p_{O_2} = 1 \times 10^{-4}$ mbar. The temperature was cycled with a heating/cooling rate of 50 K/min starting with a freshly prepared Pt(533) surface. The bar on top indicates the surface structure during heating/cooling.

at $T = 500$ K (figure 2(a)), following roughly a reaction order of 0.8 with respect to p_{O_2}. Upon decreasing p_{O_2} a very pronounced hysteresis occurs. NO formation remains roughly constant as p_{O_2} is decreased by more than one order of magnitude. In contrast N_2 production decreases quite rapidly. As a consequence the selectivity changes below 3×10^{-5} mbar from preferential N_2 production on the rising branch to preferential NO production on the falling branch of p_{O_2} variation. This strong hysteresis effect occurs only starting from the freshly prepared $4(111) \times (100)$ surface. Subsequent cycles are associated with only minor changes in the kinetics. At higher temperature, $T = 573$ K, a hysteresis still exists as demonstrated by figure 2(b), but the width of the hysteresis is considerably reduced.

The temperature dependence of the hysteresis effects becomes clearer in figure 3 showing the kinetics of the reaction as the temperature is cycled with fixed partial pressures $p_{NH_3} = 3 \times 10^{-5}$ mbar and $p_{O_2} = 1 \times 10^{-4}$ mbar. The overall picture is that N_2 production is favored at low temperature and NO production at high temperature. Practically no hysteresis effects can be found above 620 K, but below this temperature a significant hysteresis with an additional substructure in it is visible. The large hysteresis is associated with structural changes of the surface induced by the reaction. Figure 4 displays an STM image and the corresponding LEED pattern after the Pt(533) surface had been exposed to a full p_{O_2} cycle at $T = 500$ K as shown in figure 2. These images demonstrate that the reaction has caused a doubling of the step height as well as a doubling of the terrace width. These structural changes are visible directly in the STM image but also the change in the splitting of the integral order beams in the LEED pattern is consistent with the double atomic step structure.

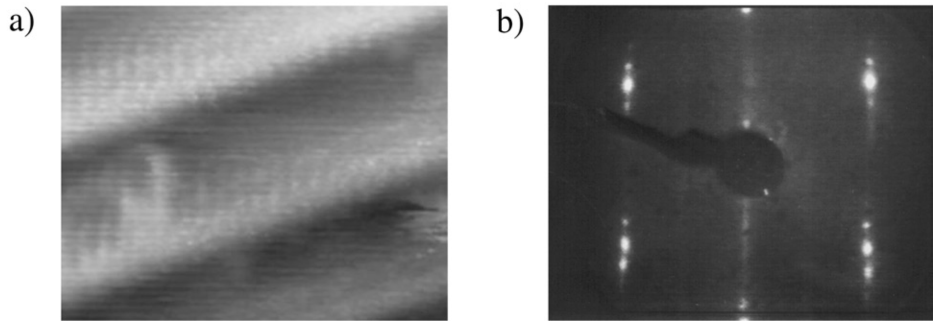

Figure 4. Structural characterization of the Pt(533) surface after reaction-induced modification of the substrate leading to a doubling in step height and terrace width. The STM image of 54×40 Å^2 in (a) was recorded with $U_t = 136$ mV and $I_t = 0.73$ nA. The LEED image in (b) was taken at beam energy $E = 88$ eV.

This doubling in step height does not occur when we expose the surface to only one of the reactants at $T \approx 500$–$600\,\mathrm{K}$ but it takes place under reaction conditions in a temperature window which extends up to $T \approx 620\,\mathrm{K}$ (in the 10^{-4} mbar range). At pressures below 10^{-5} mbar the surface step height did not change. In the hysteresis in figure 2 the surface exhibits a single atomic step structure on the rising branch of p_{O_2} cycling until close to $p_{O_2} \approx 1 \times 10^{-4}$ mbar the doubling in step height occurs. Below $T \approx 620\,\mathrm{K}$ the structural changes are practically irreversible on a time scale of minutes to 1 h as verified by LEED control experiments. As a consequence the branch of decreasing p_{O_2} is associated with the double atomic step structure, whereas on the branch of increasing p_{O_2} the surface exhibits mostly a single atomic step structure. Apparently the doubling in step height shifts the selectivity from preferential N_2 formation on the single atomic step structure to strong NO formation on the double atomic step structure.

In order to establish a relation between the *T*-dependent hysteresis in figure 3 with structural changes the *T*-cycle was interrupted at various points and LEED images were taken. The doubling in step height occurred on the heating branch above $\sim$500 K. The surface remains in this state until at $\sim$650 K the single atomic step structure forms again. During cooling the surface remains in this single atomic step structure. The dip in the N_2 production curve of the heating branch at $T \approx 580\,\mathrm{K}$ reflects the fast restructuring of the surface into double atomic steps at this temperature.

The absence of restructuring in the 500–600 K region of the cooling branch can be attributed (i) to different adsorbate coverages on the two branches of the kinetics with restructuring requiring certain adsorbate conditions and (ii) to too slow kinetics of the structural changes in comparison to the cooling rate [14]. An oxygen-induced doubling of the step height has already been noted earlier with stepped Pt(111) surfaces of (100) step orientation, but under different conditions, i.e. at $T = 1120\,\mathrm{K}$ with $p_{O_2} = 5 \times 10^{-6}$ mbar [14]. One can conclude, therefore, that a thermodynamic driving force exists for the doubling in step height given apparently by a gain in adsorption energy for oxygen on the (100) steps with double step height. A comparison of the adsorption energies of oxygen on Pt(111) and on Pt(100) does not necessarily support this assumption because similar adsorption energies around 160–200 kJ/mol are reported [15,16]. The bonding situation at step sites may, however, be quite different from that of extended single-crystal planes so that a stabilization of the double atomic step structure by a gain in oxygen adsorption energy is by no means ruled out. If the oxygen coverage is driving the restructuring then the reversal of the step height doubling at $T > 650\,\mathrm{K}$ could simply be due to a decrease in oxygen coverage at higher temperature.

As shown in earlier studies and as is also evident from chemical kinetics, a high p_{O_2} and consequently a high oxygen coverage favor NO formation against N_2 production [3,8]. If the doubling in step height is driven by a gain in oxygen adsorption energy it becomes plausible that the resulting increase in oxygen coverage should favor the NO production channel, which is what is seen in the experiment. Another important point is that NO dissociation is highly structure sensitive on Pt surfaces. Temperature-programmed desorption (TPD) experiments demonstrated that about 60% of adsorbed NO dissociates on Pt(100) during TPD, whereas almost no dissociation occurs on Pt(111) [17,18]. According to the principle of microscopic reversibility the (100) orientation should also be the one that is active in NO formation. The total amount of (100) structural units does not change in the doubling of the step height, but since the doubling in step height creates a Pt(100) micro-facet, it is again plausible as to why this structural transformation should favor NO formation.

It is quite evident that the gap between the stepped single-crystal surface studied here and the morphological changes seen with Pt/Rh gauzes in the Ostwald or Andrussow processes is quite large. Luss and Schmidt suggested that under these conditions with temperatures around 1000 °C the evaporation of volatile Pt oxides possibly in connection with a chemical transport process is the dominant mechanism for catalytic etching [19]. A free radical transport mechanism via radicals generated in the gas phase has been proposed by Phillips based on experiments with thin Pt films in ethylene/oxygen and hydrogen/oxygen mixtures [20]. Clearly the Pt surface diffusion mechanism seen here applies more to catalytic reactions under low-temperature conditions.

In summary, the results of this study show that (i) reaction-induced substrate changes shift the selectivity of the reaction and (ii) surface diffusion of Pt can lead to structural changes at low temperature. It remains to be shown what role the process studied here plays in real catalysis.

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