# CO Oxidation over a Pt(100) Surface in a Ternary Gas Mixture of CO, NO, and Oxygen

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Dedicated to Prof. Dr. Klaus Christmann on the occasion of his 65<sup>th</sup> birthday

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#### Catalysis / Carbon Monoxide / Nitrogen Monoxide / Oxygen Platinum

Catalytic CO oxidation in a ternary gas mixture of CO, NO and  $O_2$  has been studied in the  $10^{-5}$ - $10^{-4}$  mbar range using a Pt(100) sample as catalyst. Measurements of the reactive sticking coefficients of CO and NO are used to decompose the overall CO oxidation rate into the contributions from oxidation by NO and from oxidation by  $O_2$ . The experiments are complemented by simulations with a realistic 7-variable model. The surface phase transition hex  $\leftrightarrow$  $1 \times 1$  and the inhibition of NO dissociation and  $O_2$  adsorption at high adsorbate coverages lead to significant hysteresis effects.

### 1. Introduction

One of the main challenges in designing better automotive catalytic converters is to broaden the so-called  $\lambda$ -window, i.e. the range in air-to-fuel ratio,  $\lambda$ , where both, the oxidation of CO and hydrocarbons, as well as the reduction of NO<sub>X</sub>, proceed with high enough efficiency [1]. The simultaneous presence of oxidizing and reducing reactions in the three-way-catalyst (TWC) reduces the usable range of air-fuel ratios to a small window, the  $\lambda$ -window. As a simplified model system for the TWC we consider here the a Pt(100) single crystal surface in a tenary gas mixture of CO, NO, and O<sub>2</sub>. In this system essentially the reactions NO + CO  $\rightarrow$  CO<sub>2</sub> + 1/2 N<sub>2</sub> and CO + 1/2O<sub>2</sub>  $\rightarrow$  CO<sub>2</sub> occur. Both systems, the NO + CO reaction on Pt(100) and the CO + O<sub>2</sub> reaction on Pt(100) have been extensively studied because both systems exhibit interesting non-linear behavior involving oscillatory reaction rates and chemical wave patterns [2–9]. The empha-

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sis in this study, however, is not on nonlinear dynamics but on the two coexisting reaction pathways which may compete but may also profit from another via synergetic effects. The advantage of using these reactions is that both systems can be considered as well understood as evidenced by realistic mathematical models which describe rather well the experimentally observed behavior [5, 7].

The interesting nonlinear behavior of some catalytic reactions on Pt(100) is largely due to the existence of an adsorbate-driven surface phase transition which modulates the catalytic activity of Pt(100). The Pt(100) surface in its clean state exhibits a quasi-hexagonal reconstruction ("hex") of its topmost layer which can be lifted reversibly upon adsorption of CO or NO [10-12]. This constitutes an adsorbate-induced surface phase transition  $1 \times 1 \leftrightarrow$  hex which is controlled by critical adsorbate coverages. A perfect hex reconstructed surface exhibits a very low oxygen sticking coefficient and also a negligible efficiency in dissociating NO [13, 14]. For the NO + CO reaction as well as for the  $O_2$  + CO reaction the catalytically active phase is therefore the  $1 \times 1$  phase. A structurally perfect hex phase is inactive but the situation is different for the hex phase created by the  $1 \times 1 \rightarrow$  hex phase transition without high temperature annealing. On such a surface the NO reducing reactions are still quite fast and such a surface also exhibits a much higher oxygen sticking coefficient than a perfect hex phase [7, 9, 13]. The remaining high activity of this surface is attributed to structural defects in the hex phase created because the higher density of surface Pt atoms in the hex phase as compared to the  $1 \times 1$  phase requires the mass transport of about 20% of the surface Pt atoms [12].

Under reaction conditions the surface phase transition shows up in a hysteresis of the reaction rate upon cyclic variation of a parameter. As will be shown in this report in experiment and supported by mathematical modeling the presence of two reaction channels in combination with their nonlinear properties leads to a number of nontrivial effects resulting from competition as well as from synergetic interactions.

### 2. Experimental

The experiments are all conducted in a standard UHV systems equipped with a photoemission electron microscope (PEEM), a four-grid LEED optics, a scanning Auger electron spectrometer (SAES), and a differentially pumped quadrupole mass spectrometer (QMS) for rate measurements. Under reaction conditions the system is continuously pumped by a turbomolecular pump with an effective rate of app. 100 1/s. Gases are introduced via a feedback-stabilized inlet system. For recording reaction rates the sample is brought in front of a cone with a 2 mm opening behind which the partial pressures are measured by a differentially pumped QMS. Since only particles reflected from the sample surface can enter the cone opening this method also allows a direct determination of the reactive sticking coefficient of gases under reaction conditions. Denoting the signal of a

gas without reaction by  $I_0$  and during reaction with I we calculate the reactive sticking coefficient  $s_{\text{reac}}$  as

$$s_{\text{reac}} = \frac{I_0 - I}{I_0}.$$

#### **3.** The mathematical model

For catalytic CO oxidation by NO and by  $O_2$  we can formulate the following sequence of steps [2, 3]:

(R1) CO + \*  $\leftrightarrow$  CO<sub>ad</sub> (R2) NO + \*  $\leftrightarrow$  NO<sub>ad</sub> (R3) NO<sub>ad</sub> + \*  $\rightarrow$  N<sub>ad</sub> + O<sub>ad</sub> (R4) 2 N<sub>ad</sub>  $\rightarrow$  N<sub>2</sub> + 2\* (R5) CO<sub>ad</sub> + O<sub>ad</sub>  $\rightarrow$  CO<sub>2</sub> + 2\* (R6) O<sub>2</sub> + 2\*  $\rightarrow$  2O<sub>ad</sub>

(\* denotes a vacant adsorption site).

 $N_2O$  formation has been neglected in this sequence because this product only appears in larger quantities at higher pressure, above 1 mbar. The NO + CO reaction is described by steps R1–R5 to which we have to add the dissociative chemisorption of oxygen in step R6 in order that the reaction scheme also contains the three steps of the LH scheme of catalytic CO oxidation (R1, R5 and R6).

The mathematical model for the ternary system  $Pt(100)/CO+NO+O_2$  is a combination of two already existing models for Pt(100)/CO + NO and  $Pt(100)/CO + O_2$  [5, 7]. The equations were only slightly modified in order to account for the role of structural defects which are dynamically created by the phase transition and which account for a substantial part of the catalytic activity in the NO + CO reaction. The resulting 7-variable model describes the variation of the CO and NO coverages on the two surface phases, the oxygen coverage on the  $1 \times 1$  phase and the change in the substrate configuration caused by the  $1 \times 1 \leftrightarrow$  hex surface phase transition and by the creation and removal of structural defects. For both reaction systems modified mathematical models have been proposed by King et al. which differ essentially in the point that they use a power law dependence for the kinetics of the hex  $\rightarrow 1 \times 1$  surface phase transition [11, 16, 17]. In an extended model which takes into account diffusion and reaction across the  $1 \times 1/hex$  phase boundary spatiotemporal pattern formation was treated in 2D-

simulations [17]. Since the agreement with the experiment is not notably improved by this modification here the original model is employed.

We have  $\theta_{1\times 1} + \theta_{hex} + \theta_{def} = 1$  with  $\theta_{1\times 1}$  and  $\theta_{hex}$  denoting the fraction of the surface which are in the  $1 \times 1$  state and in the hex reconstructed state, respectively, and  $\theta_{def}$  representing the amount of structural defects. We assume that the structural defects are homogeneously distributed on the hex phase and that their catalytic properties are identical to the  $1 \times 1$  phase. Since we assume that their catalytic properties are identical to the  $1 \times 1$  phase we combine the two fractions according to  $\theta_{def} + \theta_{1\times 1} = \theta_{1\times 1}^{\epsilon}$ . The hex phase is catalytically inactive whereas the  $1 \times 1$  phase and the defects are active. We obtain:

$$\frac{d\theta_{\rm CO}^{\rm ixl}}{dt} = k_1 s_{\rm CO}^{\rm ixl} \theta_{\rm ixl}' p_{\rm CO} \left[ 1 - \frac{\theta_{\rm CO}^{\rm ixl}}{\theta_{\rm ixl}'} - \frac{\theta_{\rm NO}^{\rm ixl}}{\theta_{\rm ixl}'} \right] - k_2 \theta_{\rm CO}^{\rm ixl} + k_3 \theta_{\rm trap} \theta_{\rm CO}^{\rm hex} - k_4 \frac{\theta_{\rm CO}^{\rm ixl} \theta_{\rm O}^{\rm ixl}}{\theta_{\rm ixl}'}$$
(1)

$$\frac{d\theta_{\rm CO}^{\rm hex}}{dt} = k_1 s_{\rm CO}^{\rm hex} \theta_{\rm hex} p_{\rm CO} - k_5 \theta_{\rm CO}^{\rm hex} - k_3 \theta_{\rm trap} \theta_{\rm CO}^{\rm hex}$$
(2)

$$\frac{d\theta_{\text{NO}}^{|\text{x}|}}{dt} = k_6 s_{\text{NO}}^{|\text{x}|} \theta_{|\text{x}|} p_{\text{NO}} \left[ 1 - \frac{\theta_{\text{CO}}^{|\text{x}|}}{\theta_{|\text{x}|}} - \frac{\theta_{\text{NO}}^{|\text{x}|}}{\theta_{|\text{x}|}} \right] - k_7 \theta_{\text{NO}}^{|\text{x}|} + k_9 \theta_{\text{trap}} \theta_{\text{NO}}^{\text{hex}} - k_8 \frac{\theta_{\text{NO}}^{|\text{x}|} \theta_{\text{empty}}}{\theta_{|\text{x}|}}$$
(3)

$$\frac{d\theta_{\rm NO}^{\rm hex}}{dt} = k_6 s_{\rm NO}^{\rm hex} \theta_{\rm hex} p_{\rm NO} - k_{10} \theta_{\rm NO}^{\rm hex} - k_9 \theta_{\rm trap} \theta_{\rm NO}^{\rm hex}$$
(4)

$$\frac{d\theta_{\rm O}^{1\times1}}{dt} = k_{11}s_{\rm O_2}^{1\times1}\theta_{1\times1}^{'}p_{\rm O_2}\left\{ \left(1 - \frac{2\theta_{\rm CO}^{1\times1}}{\theta_{1\times1}^{'}} - \frac{2\theta_{\rm NO}^{1\times1}}{\theta_{1\times1}^{'}} - \frac{5\theta_{\rm O}^{1\times1}}{3\theta_{1\times1}^{'}}\right)^2 + \alpha \left(1 - \frac{5\theta_{\rm O}^{1\times1}}{3\theta_{1\times1}^{'}}\right)^2 \right\}$$
(5)

$$-k_{4} \frac{\theta_{CO}^{|\times|} \theta_{O}^{|\times|}}{\theta_{|\times|}^{|\times|}} + k_{8} \frac{\theta_{NO}^{|\times|} \theta_{empty}}{\theta_{|\times|}^{|\times|}} - k_{12} \frac{2\left(\theta_{O}^{|\times|}\right)}{\theta_{|\times|}}$$

$$\frac{d\theta_{1\times|}}{dt} = \begin{cases} \frac{\dot{\theta}_{CO}^{|\times|} + \dot{\theta}_{NO}^{|\times|}}{\theta_{grow}} & \text{if } \frac{\dot{\theta}_{CO}^{|\times|} + \dot{\theta}_{NO}^{|\times|}}{\theta_{grow}} > 0 \text{ and } \frac{\theta_{CO}^{|\times|} + \theta_{NO}^{|\times|}}{\theta_{grow} \dot{\theta}_{|\times|}} > 1 \\ -k_{13}\theta_{1\times|}\left(1-c\right) & \text{if } c \leq 1 \end{cases}$$

$$(6)$$

$$\frac{d\theta_{\rm def}}{dt} = \frac{d\theta_{\rm def}}{dt} = \begin{cases} -k_{14} \left(\theta_{\rm def} - \theta_{\rm perm}\right) - \dot{\theta}_{1\times 1} & \text{if} \quad \dot{\theta}_{1\times 1} \ge 0\\ -k_{14} \left(\theta_{\rm def} - \theta_{\rm perm}\right) - \beta \dot{\theta}_{1\times 1} & \text{if} \quad \dot{\theta}_{1\times 1} < 0 \end{cases}$$
(7)

with

$$\begin{aligned} \theta_{\text{trap}} &= \theta_{1 \times 1} + t_{\text{eff}} \theta_{\text{def}} \\ \theta_{\text{empty}} &= \max \left[ \left( \theta_{1 \times 1}^{\prime} - \frac{\theta_{\text{NO}}^{1 \times 1} + \theta_{\text{CO}}^{1 \times 1}}{\theta_{\text{NO,CO}}^{\text{inh}} - \frac{\theta_{\text{O}}^{1 \times 1}}{\theta_{\text{O}}^{\text{inh}}} \right), 0 \right] \\ c &= \frac{\theta_{\text{CO}}^{1 \times 1} + \theta_{\text{NO}}^{1 \times 1}}{\theta_{1 \times 1}^{\text{crit}} + \frac{\theta_{\text{O}}^{1 \times 1}}{\theta_{1 \times 1}^{\text{crit}} + \theta_{\text{O}}^{1 \times 1}} \end{aligned}$$

For a detailed discussion of the equations we refer to refs. 5 and 7. In short, the terms with  $k_1$  and  $k_2$  in Eq. 1 represent CO adsorption/desorption on the 1×1 phase, and the  $k_4$  term the reaction between CO ad oxygen (R5). The  $k_3$  term is the so-called trapping term describing the unidirectional diffusion of CO and NO adsorbed on the hex phase to 1×1 areas where they are trapped because of their higher adsorption energy. If due to trapping and adsorption the local CO/NO coverage in the 1×1 areas exceeds 0.5, then these islands grow thus maintaining a constant local coverage ( $\theta_{\text{grow}}$ ) and converting hex surface into 1×1 area. As shown experimentally by their hysteretic behavior in adsorption/desorption equilibrium CO and NO behave rather similar with respect to the surface phase transition [7]. Eqs 2 and 4 describing CO and NO, respectively, on the hex phase therefore have the same terms of adsorption, desorption, and trapping.

According to R3 NO adsorbed on the  $1 \times 1$  phase can only dissociate  $(k_8)$  if an additional vacant site is available, i. e. if  $\theta_{empty} > 0$  [7]. Atomic oxygen on the  $1 \times 1$  phase described by Eq. 5 therefore originates from two sources: adsorption of O<sub>2</sub> from the gas phase  $(k_{11})$  and NO dissociation  $(k_8)$ . Atomic oxygen is removed either through reaction with CO in step R5  $(k_4 \text{ term})$  or, at high enough temperature through thermal desorption  $(k_{12})$ . As in earlier simulations we assume that the inhibition of O<sub>2</sub> adsorption by adsorbed CO is not perfect and that a certain fraction of the surface,  $\alpha$ , therefore remains active for O<sub>2</sub> adsorption despite a high CO coverage [5]. Atomic nitrogen formed by NO dissociation is assumed to be bound only weakly and therefore the nitrogen will desorb immediately after formation.

The surface phase transition is treated in Eq. 6. The transition  $1 \times 1 \rightarrow$  hex proceeds when the local coverage in the  $1 \times 1$  area falls below a critical coverage necessary to stabilize the  $1 \times 1$  phase. The transition in the reverse direction takes place via the island growth mechanism discussed above in connection with CO/ NO trapping. The defects treated in Eq.7 are created as the surface undergoes the phase transition and they are removed either via thermal annealing ( $k_{14}$ ) or when the hex phase is converted back into the  $1 \times 1$  phase. The proportionality constant  $\beta$  determines how the rate of the phase transition  $1 \times 1 \rightarrow$  hex affects the amount of defects created. We can assume that a certain fraction of the defects,  $\theta_{perm}$ , is permanent and cannot be transformed into the hex phase. The higher efficiency of defects in CO/NO trapping is denoted by  $t_{eff}$ . Since the trapping efficiency will depend on the diffusion rate of CO and NO on the hex phase and on the surface residence time of NO/CO, this constant should be temperature dependent. In addition,  $t_{eff}$  will also vary depending on the spatial

Constant	Reaction step	$v_{\rm i} [{\rm mbar}^{-1}{\rm s}^{-1}]$
<i>k</i> <sub>1</sub>	CO adsorption	$2.21 \times 10^{5}$
<i>k</i> <sub>6</sub>	NO adsorption	$2.14 \times 10^{5}$
<i>k</i> <sub>11</sub>	O <sub>2</sub> adsorption	$4.15 \times 10^{5}$

Table 1. Temperature independent constants of the model.

The values of  $k_1$ ,  $k_6$ , and  $k_{11}$  were calculated the expression for the impingement rate of gas molecules from kinetic gas theory. The impingement rate  $\lambda_i$  is given by  $\lambda_i = p_i/(2\pi m_i kT)^{1/2}$  with  $m_i$  denoting the mass of the gas particle i. For the dissociative chemisorption in  $k_{11}$ . an additional factor of 2 has to be taken into account.

 Table 2. Sticking coefficients.

Constant	s <sub>CO</sub> <sup>hex</sup>	$s_{CO}^{1x1}$	hex S <sub>NO</sub>	$s_{NO}^{1x1}$	$s_{O_2}^{1x1}$
Value	0.78	0.91	0.91	0.91	0.3
Ref.	11	16	7	7	13, 18

Table 3. Further temperature independent constants of the model.

Constant	E <sub>rep</sub>	$\theta_O^{inh}$	$\theta_{CO, NO}^{inh}$	$\theta_O^{crit}$	$\theta_{CO, NO}^{crit}$	$\theta_{\rm grow}$	β	$t_{\rm eff}$	$\theta_{\rm perm}$	α
Value	20 kcal/ mol	0.34	0.6	0.4	0.25	0.5	$1 \times 10^{-3}$	$5 \times 10^{3}$	1×10 <sup>-6</sup>	0.01
Refs.	fit to TDS	7,16	7, 16	5, 13	5, 7, 10	5, 7, 10	fit	fit	fit	fit

separation of the defects on the hex phase which again will change depending on temperature. Since we do not know the diffusion rates on the hex phase and since we also do not know the average distance of defects from one another we neglect the temperature dependence of  $t_{eff}$ .

The constants in the simulation summarized in Table 1–3 and 4 were nearly all identical with the constants used in earlier simulations of the separate reaction systems. Only the trapping parameters and the constants concerning the defects were fitted to experimental curves. The repulsion energy,  $E_{\rm rep}$ , between CO and NO adsorbed on the 1×1 phase was determined by fitting thermal desorption spectra of CO and NO. The adsorbate coverages in the Tables 1–3 which suffice to completely suppress NO dissociation are denoted as  $\theta_0^{\rm inh}$  for the oxygen coverage and  $\theta_{\rm NO, CO}^{\rm inh}$  for the combined CO and NO coverage. The critical coverages of the adsorbates required to stabilize the 1×1 phase have been denoted as  $\theta_0^{\rm crit}$  for oxygen and  $\theta_{\rm NO, CO}^{\rm crit}$  for NO and CO.

#### 4. Results

For quantifying the contributions from the two reaction channels

- (1) CO +  $1/2O_2 \rightarrow CO_2$
- (2) NO + CO  $\rightarrow$  CO<sub>2</sub> + 1/2 N<sub>2</sub>

Constant	Reaction step	$v_{j} [s^{-1}]$	$E_{\rm j}$ [kcal/mol]	Ref.
<i>k</i> <sub>2</sub>	CO desorption $1 \times 1$	$1 \times 10^{15}$	36.8	5, 10
$k_3$	CO trapping	$1.6 \times 10^{6}$	8	fit
$k_4$	CO <sub>2</sub> formation	$2.0 \times 10^{9}$	14	5
$k_5$	CO desorption hex	$3.7 \times 10^{12}$	25.1	5, 10
<i>k</i> <sub>7</sub>	NO desorption $1 \times 1$	$1 \times 10^{16}$	36.8	7
$k_8$	NO dissociation	$2 \times 10^{16}$	28.4	7
$k_9$	NO trapping	$4 \times 10^{5}$	8	7
$k_{10}$	NO desorption hex	$1.2 \times 10^{13}$	25.1	7
<i>k</i> <sub>12</sub>	O <sub>2</sub> desorption	$3.0 \times 10^{14}$	52.1	5, 13
<i>k</i> <sub>13</sub>	phase transition $1 \times 1 \rightarrow$ hex	$2.5 \times 10^{11}$	25.3	5
$k_{14}$	defect annealing	$2.0 \times 10^{9}$	31	fit

Table 4. Temperature-dependent constants of the model.

For describing the temperature dependence of constants we assume an Arrhenius dependence  $k_i = v_i \exp(-E_i/RT)$ . The coverage dependence of the activation energy for CO and NO desorption was approximated by  $E_{ad}(\theta) = E_{ad}(0) - E_{rep}\theta^2$  where  $\theta$  is the local combined coverage of the molecular adsorbates with  $\theta = (\theta_{CO} + \theta_{NO})/\theta_{1\times 1}$  and  $E_{rep}$  is the repulsion energy of the adsorbates.

we measure the reactive sticking coefficients of CO,  $s_{CO}$  and NO,  $s_{NO}$ , and decompose the reactive sticking coefficient of CO,  $s_{CO}$ , according to the contributions of the two channels with  $s_{CO} = s_{CO}$  (NO) +  $s_{CO}$  (O<sub>2</sub>) using  $s_{CO}$ (NO) =  $s_{NO}$ .

Figure 1 displays the hysteresis we measure when a Pt(100) sample undergoes a heating/cooling cycle in a CO + NO atmosphere. Instead of the reaction rate,  $r_{CO_2}$ , we use here and in the following diagrams the reactive sticking coefficient of CO which is proportional to  $r_{CO_2}$ . The diagram in Fig. 1 shows a rate hysteresis that is connected with the structural transformation  $1 \times 1 \leftrightarrow$  hex. The hex spot intensity reflects directly the reconstructed fraction of the surface while the intensity of the integral order spot is sensitive to the surface structure as well as to the adsorbate coverages. Upon heating the reaction ignites at T = 440 K as due to desorption vacant sites are created where NO can dissociate. As the coverage upon further heating falls below the critical coverage required for stabilizing the  $1 \times 1$  phase the surface starts to reconstruct into the hex phase which is the case at 460 K. At 550 K the transformation into the hex phase is completed. Upon cooling the surface remains in the inactive hex state until CO/NO adsorption below 500 K begins to lift the hex reconstruction.

We note that during heating the catalytic activity remains substantial between 550 K and 650 K despite the formation of the supposedly inert hex phase. The upper rate branch in this T-range is metastable as one can easily demonstrate by stopping the heating schedule in this range [15]. The rate then slowly returns to the low rate branch. We therefore attribute the remaining activity in this T-range to structural defects in the hex phase which are created as result of mass transport in the  $1 \times 1 \rightarrow$  hex phase transition. The defects are slowly removed by thermal annealing thus explaining the metastable nature of this part of the rate branch.



**Fig. 1.** Hysteresis in the surface structure and in the catalytic activity upon cyclic variation of the temperature of a Pt(100) sample in a NO/CO atmosphere. Shown are the hysteresis in the LEED intensities of an integral and a fractional order beam monitoring the  $1 \times 1 \leftrightarrow$  hex phase transition and in the CO<sub>2</sub> production rate expressed here via the reactive sticking coefficient of CO. The shaded bar indicates the T-range in which the upper rate branch of the heating cycle is metastable. Heating/cooling rate 0.5 K/s.

In contrast to earlier measurements the catalytic activity on the well annealed hex phase obtained after reaching a high temperature is in fact close to zero [7]. The difference to earlier measurements is explained by the method of measuring the reactive sticking coefficient which excludes reaction from the backside of the crystal.

The simulation displayed in Fig. 2 reproduces well the experimental data, in particular, the connection of the phase transition with the rate hysteresis and the remaining high activity on the heating branch beyond 500 K. One notes that at low temperature the surface is almost completely covered by molecular NO/CO adsorbate. Ignition of the reaction at 450 K is connected with a steep drop of the coverage of the molecular adsorbates. Generated by NO dissociation simultaneously a substantial oxygen coverage develops. The structural defects created by the phase transition are responsible for the high catalytic activity persisting even after completion of the  $1 \times 1 \rightarrow$  hex phase transition. The defects are removed by thermal annealing, a process which becomes quite fast at higher temperature thus limiting the temperature range in which defects can reach a substantial



Fig. 2. Simulation of the experiment in Fig. 1 of a heating/cooling cycle of Pt(100) surface in a NO + CO atmosphere. Shown are the hysteresis in the combined NO and CO coverage and the oxygen coverage on the  $1 \times 1$  phase, the defect concentration, the amount of hex reconstruction, and the CO<sub>2</sub> production rate. Extended black regions in the curves represent kinetic instabilities. Heating/cooling rate  $\beta = 0.5$  K/s.

population. The adsorbate coverage in this range of the heating branch from 540 K to 650 K is almost zero despite a high catalytic activity. Evidently the defects have a very high efficiency of trapping NO and CO so that even with a moderate defect concentration a large part of the CO and NO molecules impinging on the surface can react to the products  $CO_2$  and  $N_2$ . The stationary adsorbate concentration remains low because NO dissociation at this high temperature is fast and no longer rate-limiting. The dark regions on the cooling branch of the reaction rate in Fig. 2 represent kinetic oscillations as described earlier [7].

When we keep the NO and CO partial pressures fixed but add oxygen with nearly one order of magnitude larger oxygen partial pressure than  $p_{\rm NO}/p_{\rm CO}$ , we



**Fig. 3.** Rate hysteresis of a Pt(100) sample in a ternary gas mixture of CO, NO and O<sub>2</sub> during a heating/cooling cycle with heating/cooling rate  $\beta = 0.5$  K/s. The reaction rate of CO<sub>2</sub> formation is expressed here via the total reactive sticking coefficient of CO,  $s_{CO}(\text{total})$ , and the contributions from oxidation via NO and O<sub>2</sub> are represented by  $s_{CO}(\text{NO})$  and  $s_{CO}(\text{O}_2)$ , respectively. Experimental conditions:  $p_{NO} = 4 \times 10^{-6}$  mbar,  $p_{CO} = 3 \times 10^{-6}$  mbar,  $p_{O_2} = 5.3 \times 10^{-5}$  mbar.

obtain the rate curves of the ternary mixture reproduced in Fig. 3. The overall reaction rate shown in the top section looks rather similar to that of the binary mixture in Fig. 1 except some fine structure on the cooling branch of the binary mixture around 450 K. The decomposition of the overall rate into the two reaction channels, however, reveals that a sharp switching of the channels takes place. The NO + CO channel is only dominant at the upper and at the lower boundary of the reactive window while in between the CO + O<sub>2</sub> channel takes over control. The reaction rate of the NO + CO channel reaches almost zero at 550 K. The first switching from the NO + CO pathway to the CO + O<sub>2</sub> channel takes place during heating at 470 K; the second switching from CO + O<sub>2</sub> back to NO + CO occurs at 580 K.



**Fig. 4.** Simulation of the rate hysteresis in catalytic CO oxidation over Pt(100) in a ternary gas mixture of CO, NO and O<sub>2</sub>. The data are simulated with nearly the same parameters as used in the experiment of Fig. 3. Shown are the defect concentration,  $\theta_{def}$ , the fraction of the surface being present as hex phase,  $\theta_{hex}$ , the CO<sub>2</sub> production rate from the CO + O<sub>2</sub> pathway,  $r_{O_2}$ , the CO<sub>2</sub> production rate from the NO + CO pathway,  $r_{NO}$ , and the total CO<sub>2</sub> production rate,  $r_{CO_2}$ . The corresponding reactive sticking coefficients of CO for the different pathways of CO oxidation are displayed on the right side of the diagram.

The simulation reproduced in Fig. 4 explains why this twofold switching of the reaction channel takes place. The "surface explosion" of the NO + CO reaction at 430 K creates a largely adsorbate free  $1 \times 1$  surface where O<sub>2</sub> can adsorb uninhibitedly. Due to a nearly 10fold excess of oxygen in the gas phase which overcompensates the much lower oxygen sticking coefficient of oxygen as compared to NO, the CO + O<sub>2</sub> channel takes control. The NO + CO channel gains back control when the  $1 \times 1 \rightarrow$  hex phase transition occurs at 570 K. The defects on the hex phase are evidently not very active in the CO + O<sub>2</sub> reaction while due to trapping of both, NO and CO, the NO + CO reaction can still proceed very efficiently on a hex reconstructed surface which has not been annealed. Only when at high temperature the defect concentration becomes very small due to thermal annealing the catalytic activity approaches zero. The defects on the



**Fig. 5.** Variation of the overall reaction rate and of the different reaction channels in a ternary mixture of CO, NO and O<sub>2</sub> as  $p_{O_2}$  is cycled. The hysteresis are probably not real but originate from saturation of the chamber walls. Experimental conditions: T = 479 K,  $p_{NO} = 4 \times 10^{-6}$  mbar,  $p_{CO} = 3 \times 10^{-6}$  mbar,  $dp/dt = 9.3 \times 10^{-7}$  mbar/s.

hex phase are therefore responsible for the switching from the CO +  $O_2$  pathway to the NO + CO channel at 580 K. Since the defects on the hex phase presumably exhibit an oxygen sticking coefficient comparable to that of the 1×1 phase one should suspect that also the contribution from the CO +  $O_2$  channel remains substantial in the T-range where the catalytic activity is controlled by defects. The dominance of the NO + CO channel can only be explained by the very high NO/CO trapping efficiency of defects. Compared to NO and CO the diffusivity of atomic oxygen on Pt is much lower and consequently also the trapping efficiency of oxygen will be much lower.

Upon cooling the activity remains very low until below 500 K CO/NO adsorption starts to lift the hex reconstruction. Since the local adsorbate concentration in the 1×1 islands remains high dissociative O<sub>2</sub> adsorption cannot compete against the molecular adsorption of CO and NO. NO can still dissociate because the inhibition coverage for NO dissociation,  $\theta_{inh}$ , is with  $\theta_{inh} = 0.6$  above the local adsorbate coverage in the growing 1×1 islands,  $\theta_{grow}$  which is 0.5 in the simulation. Therefore the NO + CO channel dominates in this part of the Tcycling experiment over the CO + O<sub>2</sub> channel. When at even lower temperature NO dissociation is finally suppressed by a high adsorbate coverage the surface activity dies away.



**Fig. 6.** Simulation of the experiment in Fig. 5 demonstrating the dependence of the overall reaction rate and of the different reaction channels on the oxygen partial pressure. Shown are the oxygen and NO coverage on the  $1 \times 1$  phase, the total reactive sticking coefficient of CO and the contribution of the NO + CO channel to the reactive sticking coefficient of CO. The selectivity towards the NO + CO pathway is defined in the same way as in Fig. 5. Note that a slightly higher temperature than the temperature in the experiment had to be used in order to reproduce the experimentally observed behavior. Parameter values: T = 500 K,  $p_{NO} = 4 \times 10^{-6}$  mbar,  $p_{CO} = 3 \times 10^{-6}$  mbar,  $dp/dt = 5 \times 10^{-7}$  mbar/s.

In order to systematically investigate the influence of  $O_2$  on the reaction the oxygen partial pressure was cycled at fixed temperature T = 480 K and with  $p_{NO}$  and  $p_{CO}$  being fixed at the values of the previous experiment. The resulting diagram displayed in Fig. 5 shows an overall reaction rate that is nearly independent of  $p_{O_2}$ . With increasing  $p_{O_2}$  the contribution of the NO + CO channel decreases monotonically from 100% at  $p_{O_2} = 0$  to only 10% when  $p_{O_2}$  reaches  $9 \times 10^{-5}$  mbar; the corresponding CO +  $O_2$  fraction (not shown) rises from zero to 90%. The simulation in Fig. 6 reproduces this behavior rather well. The continuous transition can be attributed to the absence of the phase transition. At 500 K with intermediate adsorbate coverages the  $1 \times 1$  phase remains stable and both reaction pathways are active in this coverage range. As a consequence, it is



**Fig. 7.** Variation of the overall reaction rate and of the different reaction channels in a ternary mixture with as  $p_{O_2}$  is cycled. In comparison to the previous experiment in Fig. 5 CO is now in excess compared to NO. Shown are the reactive sticking coefficient of oxygen,  $s_{O_2}$ , and the different contributions to the reactive sticking coefficient of CO with  $s_{CO}(NO)$  and  $s_{CO}(O_2)$ , representing the contributions from the NO + CO and the CO + O<sub>2</sub> pathway, respectively. Experimental conditions: T = 420 K,  $p_{NO} = 2 \times 10^{-6}$  mbar,  $p_{CO} = 3 \times 10^{-6}$  mbar,  $dp/dt = 9.3 \times 10^{-7}$  mbar/s.

essentially the partial pressure ratio NO : O<sub>2</sub> which dictates which channel is preferred.

A qualitatively different behavior is found when CO in the CO + NO mixture is in excess. For  $p_{NO}$ :  $p_{CO}$  = 2:3 and at lower temperature, at 420 K, one obtains the diagram displayed in Fig. 7. A broad rate hysteresis is seen but in contrast to the previous diagrams the hysteresis here is not caused by the phase transition since the substrate remains in a  $1 \times 1$  configuration all the time. Rather the hysteresis is caused by the inhibitory effects of large adsorbate coverages on the reaction as demonstrated by the simulation shown in Fig. 8. At low  $p_{O_2}$  NO dissociation is blocked because on a surface fully packed with adsorbates no vacant sites are available. With increasing  $p_{O_2}$  initially the surface remains inactive until at  $p_{O_2} = 4.5 \times 10^{-5}$  mbar the reaction ignites. In the simulation the triggering is caused by the alpha-term in Eq. 5 supposedly representing surface defects where adsorbed CO cannot inhibit O<sub>2</sub> adsorption. The triggering of the reaction lowers the adsorbate coverage far enough so that now both reaction channels become active, the NO + CO and the CO + O<sub>2</sub> pathway. Upon further increasing  $p_{O_2}$  the oxidation by  $O_2$  becomes more and more dominant. In the direction of decreasing  $p_{O_2}$  the active state of the surface is maintained down to  $5 \times 10^{-6}$  mbar until the transition to an adsorbate poisoned surface occurs. The



**Fig. 8.** Simulation of the experiment in Fig. 7 showing the dependence of the overall reaction rate and of the different reaction channels as  $p_{O_2}$  is varied. Shown are the CO coverage on the  $1 \times 1$  phase, the reactive sticking coefficient of oxygen,  $s_{O_2}$ , and the different contributions to the reactive sticking coefficient of CO with  $s_{CO}(NO)$  and  $s_{CO}(O_2)$ , representing the contributions from the NO + CO and the CO + O<sub>2</sub> pathway, respectively. The total reactive sticking coefficient of CO is denoted as  $s_{CO}(total)$ . Parameter values: T = 418 K,  $p_{NO} = 2 \times 10^{-6}$  mbar,  $p_{CO} = 3 \times 10^{-6}$  mbar,  $dp/dt = 2.5 \times 10^{-8}$  mbar/s.

simulation in Fig. 8 which reproduces the experiment reveals that essentially the build-up of a large CO coverage is responsible for the rate hysteresis.

## 5. Conclusions

The competition between two CO oxidation channels has been investigated with a ternary reaction mixture of CO, NO and  $O_2$  and with a Pt(100) surface as model catalyst. The adsorbate-induced surface phase transition and the inhibitory effect of large adsorbate coverages on NO- dissociation and  $O_2$  adsorption deter-

mine the catalytic activity of the surface. Upon heating up the Pt(100) surface the main reaction channel switches from oxidation by NO to oxidation by O<sub>2</sub> and then back to oxidation to NO. The latter switching occurs because on a freshly formed hex phase the catalytic activity in the NO + CO channel remains high due to structural defects trapping CO and NO and dissociating NO. Synergetic effects between the two reaction channels have been observed as well. Since both reaction channels are blocked by high adsorbate coverages ignition of one reaction channel will automatically also start the reaction in the second channel. The critical point for a further refinement of the model is clearly obtaining a more detailed knowledge about the nature of the structural defects and their spatial distribution.

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