

Chapter 3

Steady state and rate-determining step

Abstract We present a set of experiments where the activity is measured at steady state at different surface temperatures and fractions of CO in the reactant flux. Two reaction regimes are discriminated. A kinetic bistability is only observed on Sample C. A mean field model simulates the experiments. It allows us to find the degree of rate control (DRC) of the elementary steps in the reaction network. This parameter is of general importance and is used to understand the results of the following chapters.

3.1 CO₂ production at steady state as a function of x_{CO} and T

In a first step, we measure the global CO₂ production at steady state with AI QMS. O₂ (99.9995%, Linde AG) and CO (99.997%, Linde AG, purified by a Waferpure MiniXL WPMV200CO Mycrolis GmbH filter) are provided by the EBs. The total flux is kept constant and equal to $2.9 \times 10^{-14} \text{ cm}^{-2} \text{ s}^{-1}$. The fluxes F_{O_2} and F_{CO} are varied systematically such that the sum of the effective partial pressures at the sample position is constant and equal to 10^4 Pa . The fraction of CO in the total flux is defined as

$$x_{\text{CO}} \equiv \frac{F_{\text{CO}}}{F_{\text{O}_2} + F_{\text{CO}}}.$$

The results obtained with Samples A, B and C are displayed in Figure 3.1. Two reaction regimes are discriminated versus x_{CO} . For low x_{CO} , the CO₂ production at steady state increases linearly with x_{CO} , exhibiting first order kinetics. We call this regime O-rich. It is rather independent of surface temperature T . The CO₂ production then reaches a maximum, after which the rate decreases due to the decreasing supply in O₂. This defines the so-called CO-rich regime. For high T , the CO₂ production is inversely proportional to x_{CO} and is close to inverse first order reaction kinetics. For lower T , however, the reaction rates are very low, which we attribute to poisoning of the surface by CO_{ad}. Furthermore, a kinetic bistability is observed on Sample C for $T < 440 \text{ K}$.

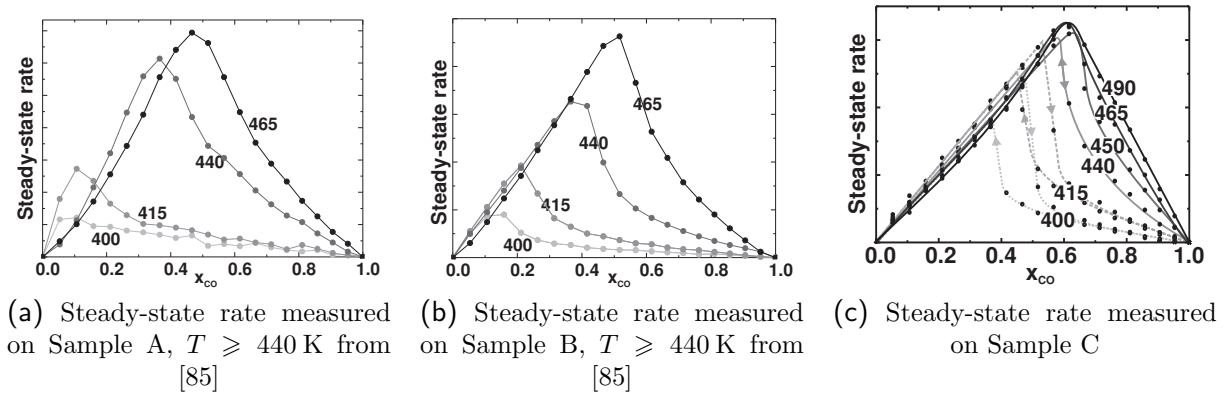


Figure 3.1. Steady-state rates on samples A, B and C .

3.2 Establishment of the homogeneous mean field model

In order to gain more informations from the experiments and to calculate the rate-determining steps (RDSS) of the reaction, we utilize the mean field (MF) model derived by Hoffmann in Refs. [85,86]. The model is briefly recalled in this section.

Reaction network Heterogeneous catalytic reactions can occur through a limited number of steps:

1. adsorption of molecules from the gas phase at the catalyst surface;
2. diffusion of adsorbates at the surface;
3. desorption of products and/or reactants to the gas phase;
4. reaction between adsorbates or between adsorbates and the gas phase.

For simple cases, these steps can be described by rate equations. Let us derive these equations and establish the homogeneous mean field model (HoMF).

Lattice–gas model A model for the description of adsorbates at a surface is the lattice–gas model. The support is represented as a net of sites at which molecules from the gas phase adsorb. Diffusion then consists in hopping from one site to its nearest neighbor, and interactions between nearest neighbors lead to reaction. Each step occurs according to its probability defined by kinetic rate equations. Consequently, a numerical treatment of such a model implies to explicitly take each site into account. It then usually requires the use of stochastic algorithms like Monte Carlo. The main drawback is that these calculations become numerically very expensive on larger scales.

Process	Chemical Eq.	Rate s ⁻¹
Adsorption of CO	$\text{CO}_g \xrightarrow{k_{\text{CO}}^{\text{ad}}} \text{CO}_{\text{ad}}$	$w_{\text{CO}}^{\text{ad}}(\Theta_{\text{O}}, \Theta_{\text{CO}})$
Desorption of CO _{ad}	$\text{CO}_{\text{ad}} \xrightarrow{k_{\text{CO}}^{\text{des}}} \text{CO}_g$	$w_{\text{CO}}^{\text{des}}(\Theta_{\text{O}}, \Theta_{\text{CO}})$
Adsorption of O ₂	$\text{O}_{2g} \xrightarrow{k_{\text{O}_2}^{\text{ad}}} 2\text{O}_{\text{ad}}$	$w_{\text{O}_2}^{\text{ad}}(\Theta_{\text{O}}, \Theta_{\text{CO}})$
Reaction	$\text{CO}_{\text{ad}} + \text{O}_{\text{ad}} \xrightarrow{k_{\text{LH}}} \text{CO}_{2g}$	$w_{\text{LH}}(\Theta_{\text{O}}, \Theta_{\text{CO}})$

Table 3.1. The four elementary steps of the Langmuir-Hinshelwood mechanism of CO oxidation on noble metals in terms of propensity functions.

Mean field model A MF treatment is then more adapted. Let us consider a single adsorbate in the lattice–gas model. The interaction of this molecule with all other adsorbed species results in a single component, which is the average of all two-bodies interactions of this molecule with the others. Hence the name MF: a molecule is taken in a continuum field, which consists of the mean value of all interactions with this molecule [87]. Since every step of the reaction network is treated on average on a single molecule, the method is not dependent on the size of the system, which can be considered infinite (i.e. a single crystal). The adsorbates are seen on average over the surface layer, the relevant quantity is thus the coverage Θ_i , defined as the number of adsorbed molecules N_i per surface atom N_{Support}

$$\Theta_i \equiv \frac{N_i}{N_{\text{Support}}}. \quad (3.1)$$

One major drawback to this approximation is that surface order is ignored, where it is known to play an important role in heterogeneous catalysis.

Propensity function Chemical rate equations (or propensity functions [20], unit s⁻¹) indicate the propensity of the surface to change its state Θ according to one step j of the reaction network. It is defined as a function $w_j(\Theta)$. Establishment of a MF model consists in deriving the propensity functions relevant to the reaction network. The oxidation of CO on noble metals is well established [6] and can be decomposed in the elementary processes in Table 3.1, cf. Section 1.3.

3.2.1 Surface phenomena

Adsorption

Adsorption can be understood as the reaction between a free surface site and a molecule from the gas phase. CO adsorbs non dissociatively and O₂ adsorbs dissociatively at the surface,



The adsorption probability k_i^{ad} of a molecule i is proportional to the flux F_i and the sticking coefficient S_i

$$k_i^{\text{ad}} = \frac{F_i}{N_{\text{Support}}} S_i.$$

The propensity functions are then

$$w_{\text{CO}}^{\text{ad}}(\Theta) = \frac{F_{\text{CO}}}{N_{\text{Pd}}} S_{\text{CO}}$$

$$w_{\text{O}_2}^{\text{ad}}(\Theta) = \frac{2F_{\text{O}_2}}{N_{\text{Pd}}} S_{\text{O}_2}.$$

The flux is defined as the number of molecules passing through an area in a given time (unit $\text{m}^{-2} \text{s}^{-1}$). The flux at a surface, or impingement rate, can be calculated using the kinetic gas theory [61] as

$$F_i = \frac{p_i}{\sqrt{2\pi\mathcal{M}_i kT}},$$

with p_i pressure and \mathcal{M}_i the mass of a molecule i .

The sticking coefficient $S_i \equiv S_i^0 f(\Theta)$ defines the probability of a molecule hitting the surface to remain in the adsorbate state. S_i^0 is the initial sticking coefficient, i.e., sticking coefficient on a clean surface and $f(\Theta)$ can be any function of the coverages. The sticking coefficient can assume any value between 0 and 1 and has no unit. It is modeled here using simple (but not always realistic) Langmuir laws,

$$S_{\text{CO}} = \begin{cases} S_{\text{CO}}^0 \left(1 - \frac{\Theta_{\text{CO}}}{\Theta_{\text{CO}}^{\text{max}}} - C_T \frac{\Theta_{\text{O}}}{\Theta_{\text{O}}^{\text{max}}}\right) & \text{if } f(\Theta) > 0 \\ 0 & \text{if } f(\Theta) \leq 0 \end{cases}, \quad (3.2)$$

$$S_{\text{O}_2} = \begin{cases} S_{\text{O}_2}^0 \left(1 - \frac{\Theta_{\text{CO}}}{\Theta_{\text{CO}}^{\text{max}}} - \frac{\Theta_{\text{O}}}{\Theta_{\text{O}}^{\text{max}}}\right)^2 & \text{if } f(\Theta) > 0 \\ 0 & \text{if } f(\Theta) \leq 0 \end{cases}. \quad (3.3)$$

A correction C_T is introduced concerning the influence of O_{ad} on the sticking coefficient of CO, which is physically related to the presence of a precursor to CO chemisorption [88]. The poisoning effect of preadsorbed CO_{ad} on the sticking coefficient of O_2 is also introduced.

Diffusion

Diffusion consists in the displacement of adsorbates at the surface from site to site. MF models do not describe actual sites and therefore do not treat diffusion correctly in principle. The fact that adsorbates are seen on average over the surface implies infinitely fast diffusion of every adsorbate. This constitutes a drastic approximation and diffusion can still be added to the model by means of reaction–diffusion schemes, as done in Chapter 4.

Desorption

Adsorbates, either reactants or products, may desorb to the gas phase. O_{ad} does not desorb in the temperature range studied and desorption of CO_{2ad} is fast compared to its formation [46]. Desorption of O_{ad} and CO_{2ad} are therefore not taken into account explicitly.

The desorption rate $w_{CO}^{des}(\Theta)$ for CO_{ad} is expressed as a function of the coverages and of the rate constant k_{CO}^{des} as

$$w_{CO}^{des}(\Theta) = k_{CO}^{des} \Theta_{CO}.$$

An Arrhenius T dependence

$$k_{CO}^{des} = \nu_{CO}^{des} \exp\left(-\frac{E_{CO}^{des}}{RT}\right), \quad \text{with} \quad E_{CO}^{des} = E_{CO}^{des 0} \left(1 - \beta \frac{\Theta_{CO}}{\Theta_{CO}^{max}}\right),$$

is assumed for the rate constant. β corrects the desorption energy at zero coverage $E_{CO}^{des 0}$ to render CO_{ad} poisoning within the most simple approximation of a linear dependence on the coverage.

Reaction

Two reaction mechanisms are relevant to heterogeneous catalysis: two adsorbates react at the surface (Langmuir-Hinshelwood, LH) and one molecule from the gas phase reacts with an adsorbate (Eley-Rideal). CO oxidation on Pd is known to react according to a LH mechanism [6]. Thus CO_2 formation occurs through the adsorbate states of the reactants and

$$w_{LH}(\Theta) = k_{LH} \Theta_{CO} \Theta_O, \quad \text{with} \quad k_{LH} = \nu_{LH} \exp\left(-\frac{E_{LH}}{RT}\right)$$

an Arrhenius T dependence.

3.2.2 Rate equations (HoMF)

The variations of coverages in time are then expressed as the weighted sum of the LH steps given in Table 3.1,

$$\frac{d\Theta_{CO}}{dt} = w_{CO}^{ad}(\Theta_O, \Theta_{CO}) - w_{CO}^{des}(\Theta_{CO}) - w_{LH}(\Theta_O, \Theta_{CO}), \quad (3.4a)$$

$$\frac{d\Theta_O}{dt} = 2w_{O_2}^{ad}(\Theta_O, \Theta_{CO}) - w_{LH}(\Theta_O, \Theta_{CO}). \quad (3.4b)$$

Integration of the ordinary differential equations (ODEs) Eq. 3.4 leads to the MF representation of the reaction (HoMF).

3.2.3 Validation of the model

The parameters for HoMF not available from the literature are obtained by fitting to the experiments. By definition, the model describes more accurately experiments performed

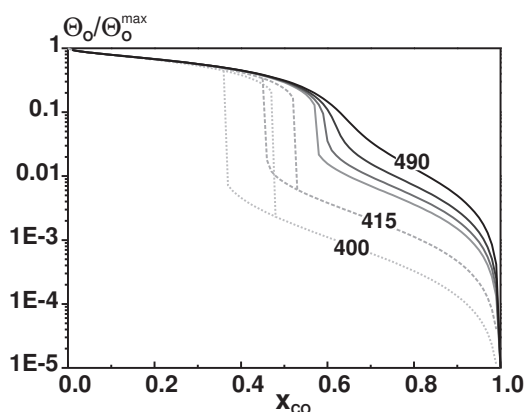
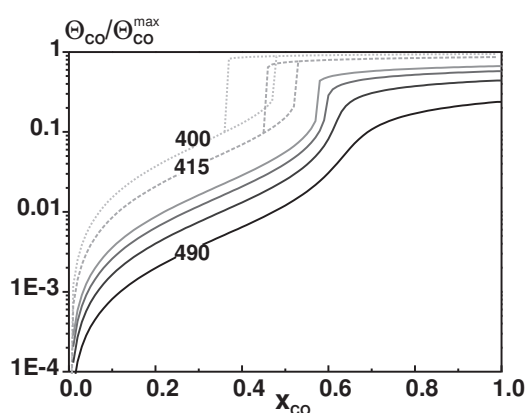
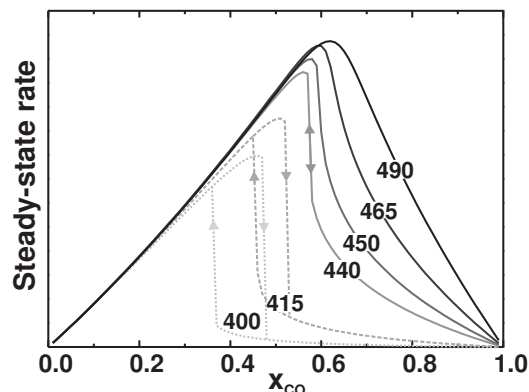
(a) HoMF; Θ_O/Θ_O^{\max} (b) HoMF; $\Theta_{CO}/\Theta_{CO}^{\max}$ (c) HoMF; \mathcal{R}

Figure 3.2. (c) Fitting of the experiments Figure 3.1 by HoMF from which the coverages at steady state (a) and (b) are extracted as a function of x_{CO} and for $T = 400, 415, 440, 450, 465$ and 490 K.

on larger surfaces. We therefore chose the experiments on Sample C as reference. Figure 3.2c shows the resulting fit with parameters given in Table 3.2. Comparison with Figure 3.1 shows that HoMF accurately reproduces the experiments. Also note that Sample B was the reference in [86] and some parameters change.

The coverages are directly available from the model (Figure 3.2a and b) and this brings a new definition for the O-rich and CO-rich regimes: The O-rich regime is characterized by low Θ_{CO} and high Θ_O . Conversely, the CO-rich regime is characterized by high Θ_{CO} and low Θ_O .

3.3 Rate-determining step

The rate-determining step (RDS) is commonly used to describe the kinetics of reaction mechanisms in catalysis. It refers to the slowest step of the reaction network, and therefore controls the activity. Campbell [90] gives a simple way to calculate RDSs from MF models.

Parameter	Numerical value	Reference
N_{Pd}	$1.53 \times 10^{19} \text{ m}^{-2}$	
p	$1.0 \times 10^{-4} \text{ Pa}$	Experimental
T_{vel}	300 K	Experimental
\mathcal{M}_{CO}	$28.010 \text{ kg mol}^{-1}$	
\mathcal{M}_{O}	$31.999 \text{ kg mol}^{-1}$	
C_T	0.3	Fit
β	0.12	Fit
S_{CO}^0	0.7	[89]
$S_{\text{O}_2}^0$	$1.0 - 7.4 \times 10^{-4} \cdot T$	Fit, [89]
$E_{\text{CO}}^{\text{des}}$	142 kJ mol^{-1}	Fit, [64, 89]
$\nu_{\text{CO}}^{\text{des}}$	$4.0 \times 10^{14} \text{ s}^{-1}$	Fit, [64, 89]
E_{LH}	53 kJ mol^{-1}	Fit, [46, 64]
ν_{LH}	$5.0 \times 10^7 \text{ s}^{-1}$	Fit, [64]

Table 3.2. Numerical parameters used for HoMF, also see [86].

3.3.1 Degree of rate control

Definition The degree of rate control (DRC) is a mathematical tool to determine RDSs from microkinetic models. The DRC $X_{\text{rc},j}$ is the variation $\delta\mathcal{R}$ in the overall reaction rate at steady state resulting from an infinitesimal variation $\delta k_j/k_j$ of the rate constants for one step j and its reverse step. Both directions (forward and backward) have to be changed at the same time in order to leave the equilibrium constant unchanged. The DRC is then simply

$$X_{\text{rc},j} \equiv \frac{k_j}{\mathcal{R}} \frac{\delta\mathcal{R}}{\delta k_j}.$$

According to Campbell, this brings more rigorous definitions for the RDS,

- a step of the mechanism is the RDS if and only if $X_{\text{rc},j} \approx 1$,
- it is an inhibition step (IS) if and only if $X_{\text{rc},j} < 0$.

Remarks and limitations However, a strict application of the DRC cannot be applied in the case of CO oxidation in the temperature range studied:

- The reaction is bistable. Therefore, in some cases $\delta\mathcal{R}$ calculated is not the change due to a variation of the rate constants but to the switching of the reaction to the other stable state.
- O_{ad} does not desorb below 700–800 K. Therefore, the rate constant for O_2 adsorption is changed, but not its reverse step. The equilibrium constant is displaced for the calculation of the DRC for O_2 adsorption–desorption.

- $\text{CO}_{2\text{ad}}$ desorbs immediately after its formation and does not adsorb in measurable quantities on the metal. Adsorption of CO_2 is therefore not taken into account in the model. The equilibrium constant for the reaction is also displaced.

The effect of the displacement of the equilibrium is assumed to be negligible in the case of a sufficiently small $\delta k_j/k_j$. For the bistability, however, the method fails and the results cannot be interpreted as relevant to RDSSs.

3.3.2 Determination of the RDS

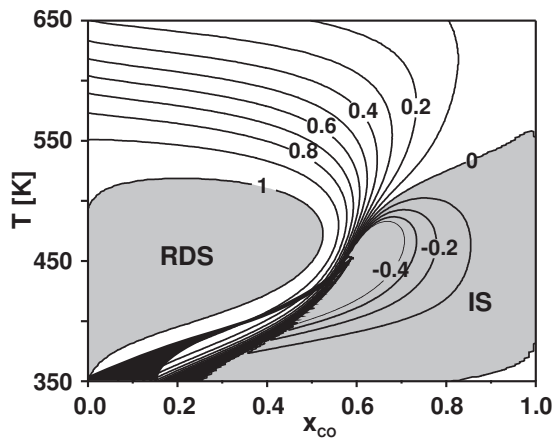
Figure 3.3 displays the DRC of each step of CO oxidation on Pd calculated with HoMF. The DRCs are calculated for surface temperatures in the range $350 \leq T \leq 650$ K and for $0.0 < x_{\text{CO}} < 1.0$ at constant total pressure. The RDS and IS for each DRC are represented as the gray areas on the contour plots.

Bistable regime The fact that the method fails in the bistable regime can be used to identify under which conditions the reaction is bistable. It also gives an idea of the relative stability of each state. If a small change of the rate constants switches the reaction to the other regime, it can be considered that a thermodynamically metastable state is in competition with a stable state. From Figure 3.3, we find bistability of the reaction up to 450 K. The region expands from $0.0 \leq x_{\text{CO}} \leq 0.25$ at $T = 350$ K to $x_{\text{CO}} = 0.6$ at $T = 450$ K. It is also noticeable that more metastability is found at lower temperatures. Experimentally, this means that small variations in the conditions would immediately induce a change in the reaction rate. This would likely accounts for the existence of chemical waves [91] or fluctuations of the reaction rate (Chapter 6) in the metastable regime.

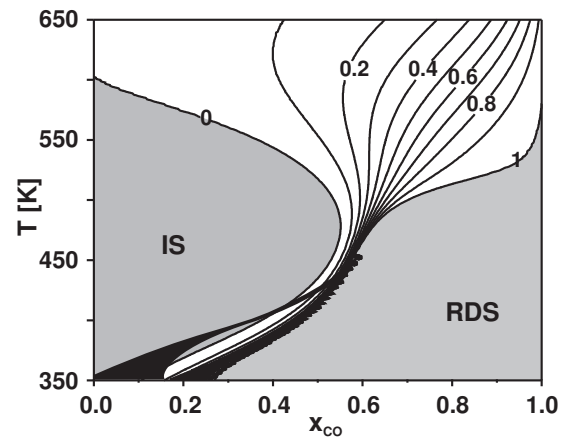
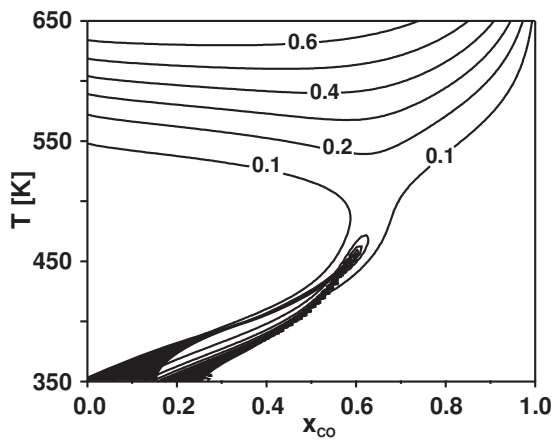
Adsorption–desorption We compare the DRCs for CO adsorption–desorption (Figure 3.3a) and O_2 adsorption (Figure 3.3b) as they exhibit complementary features:

O-rich regime For low x_{CO} and $T \leq 480$ K, adsorption of CO is the RDS of the reaction and adsorption of O_2 has no significant effects ($X_{\text{rc}} \approx 0$). Here in the O-rich regime, Θ_{CO} increases with the CO adsorption probability. Then, due to the first order kinetics there, the reaction rate increases as well. However, O_2 is supplied in excess so that Θ_{O} already has its maximum equilibrium value. A small change in the adsorption probability of O_2 has then little effect on Θ_{O} and on the reaction rate.

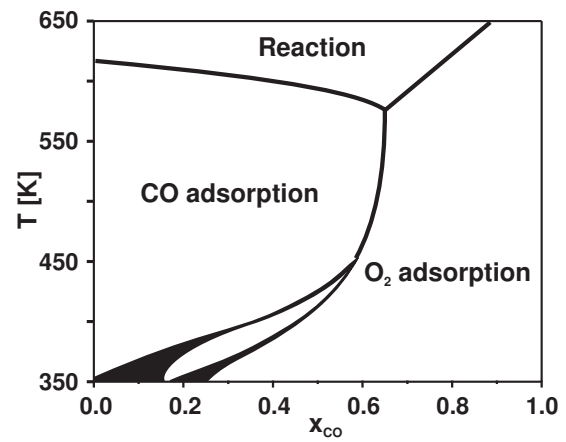
CO-rich regime In a comparable temperature range, in the CO-rich regime, adsorption of CO becomes a strong inhibitor of the reaction, whereas O_2 adsorption is the RDS. This accounts for the inhibition of O_2 adsorption by large Θ_{CO} (Eq. 3.2). It reflects the CO_{ad} poisoning observed experimentally. In this regime, Θ_{CO} reaches its maximum equilibrium value. A decreasing probability for CO adsorption or an increasing probability for O_2 adsorption have therefore the same effect of increasing Θ_{O} , either by decreasing the poisoning effect or because Θ_{O} is low under these conditions. It then results in an increase of the reaction rate. The inhibiting effect



(a) HoMF; Adsorption-desorption of CO

(b) HoMF; Adsorption of O₂

(c) HoMF; Reaction



(d) HoMF; Highest degree of rate control

Figure 3.3. Degrees of rate control. Calculations from HoMF ($\Delta t = 0.1$ ms, $\delta k_j/k_j = 10^{-6}$). RDS stands for rate-determining step and IS for inhibition step as defined in [90]. The area in black in the bottom left corner of the plots is where the reaction switches to the other steady state upon changing the rate constants.

Reaction regime	O-rich	CO-rich
Kinetics	1 st order with p_{CO}	complex for low T , 1 st order with p_{CO} for $T > 440$ K
Surface state	high Θ_{O} , low Θ_{CO}	low Θ_{O} , high Θ_{CO}
RDS	CO ads.–desorption	O ₂ adsorption

Table 3.3. Main characteristics of the O-rich and CO-rich regimes.

of CO_{ad} disappears for $T \geq 500$ K, where the measured reaction rate is again first order. This is attributed to an increasing desorption probability of CO_{ad} with T .

Surface poisoning and RDS Refs. [88,92] show that adsorption of CO is started from a weakly bound precursor state with a low steady-state coverage. Chemisorption occurs from this precursor state with a high probability and a weak dependence on the surface state (coverages of either CO_{ad} or O_{ad}). Therefore, when CO adsorption is the RDS, there is no O_{ad} poisoning of the reaction. However, dissociative adsorption of O_2 is strongly inhibited by CO_{ad} . When O_2 adsorption is the RDS, the reaction rate is still dependent on Θ_{CO} .

Reaction In the temperature range studied, reaction is never RDS nor IS. For $T \leq 550$ K, small changes in the reaction probability have no effects on the reaction rate ($0.0 < X_{\text{rc}} < 0.1$, Figure 3.3c). The reaction rate is then totally determined by the adsorption probabilities of CO and O_2 . Still, the DRC for reaction increases with T and becomes the largest for $T \geq 600$ K (Figure 3.3d).

The overall small DRC for reaction is expected from the small activation energy of this step (about one third of the activation energy for CO_{ad} desorption, Table 3.2). Concerning the T dependence, it is noticeable that the desorption probability for CO_{ad} increases faster with T than the reaction probability. The sticking coefficients for CO and O_2 , which govern the adsorption probabilities, are rather T independent at steady state. In consequence, at higher temperatures, CO_{ad} desorption becomes relatively faster than reaction and the reaction rate depends more on the LH step. Another general trend for the DRC of reaction is that it is rather independent of x_{CO} over the whole temperature range. This behavior is expected from a LH type reaction mechanism, where the reaction probability only depends on the quantity of adsorbed species and not on the gas phase, whereas x_{CO} is primarily defined as the gas phase composition.

3.4 Summary

The experiments exhibit two reaction regimes, which can be characterized by means of the microkinetic model, see Table 3.3.

It is important to underline the role of Θ_{CO} on the activity under all conditions: In the O-rich regime, adsorption–desorption of CO is the RDS, it is related of Θ_{CO} . Whereas

in the CO-rich regime, adsorption of O_2 is the RDS. But here again this step depends on Θ_{CO} via CO_{ad} poisoning.