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High-pressure STM studies of oxidation catalysis

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Chapter 2

Introduction to the theory concerning CO oxidation over platinum group metals

In this chapter a review is given of the literature about CO oxidation on platinum group metals surfaces. First we discuss the CO interaction with these metals, and then we describe the mechanisms behind the CO oxidation on Pt-group metals and the oscillatory behaviour of this reaction.

2.1 CO interaction with platinum group metals

The interaction of CO with platinum group metals has been intensely studied in the last decades [1-3]. It is generally accepted today that carbon monoxide adsorbs as a molecule on such a metal with the carbon atom directed towards the surface and that it can coordinate in several geometries. The CO bonding to metal surfaces is described in the terms of the so-called Blyholder model, which invokes a donor-acceptor mechanism [4]. In this model the bonding occurs through a concerted electron transfer from the highest filled (5σ) molecular orbital of CO to unoccupied metal orbitals (essentially d orbitals), with back-donation occurring from occupied metal orbitals to the lowest unfilled (2π) orbital of CO (Fig. 2.1). The strength of the CO-metal bond might be expected to depend upon: 1) the nature of the adsorbent metal, 2) the crystallographic orientation of the surface, and 3) the geometric location of the adsorbed molecule on a given single crystal plane [5, 6]. Pavão and collaborators are given an excellent review regarding the early pioneering work of Blyholder and the improvements made in the following years by the means of quantum chemical calculations [7].

The three typical, symmetric adsorption positions for CO molecules that are usually considered on a metal terrace are 1) “on-top”, the CO standing up on top of a metal atom, 2) “bridge-bonded”, the CO being adsorbed above a position midway between two metal atoms and 3) “threefold-coordinated”, the CO placed at above a position symmetrically between three atoms of the metal substrate. On the dense (111) and (100) surfaces of the FCC metals, CO prefers the on-top and bridge positions above the high coordination of the threefold adsorption geometry. On rhodium and platinum, CO adsorbs more strongly in the on-top position than in the bridge position, while on nickel and palladium the bridge position forms the stronger bond [8].

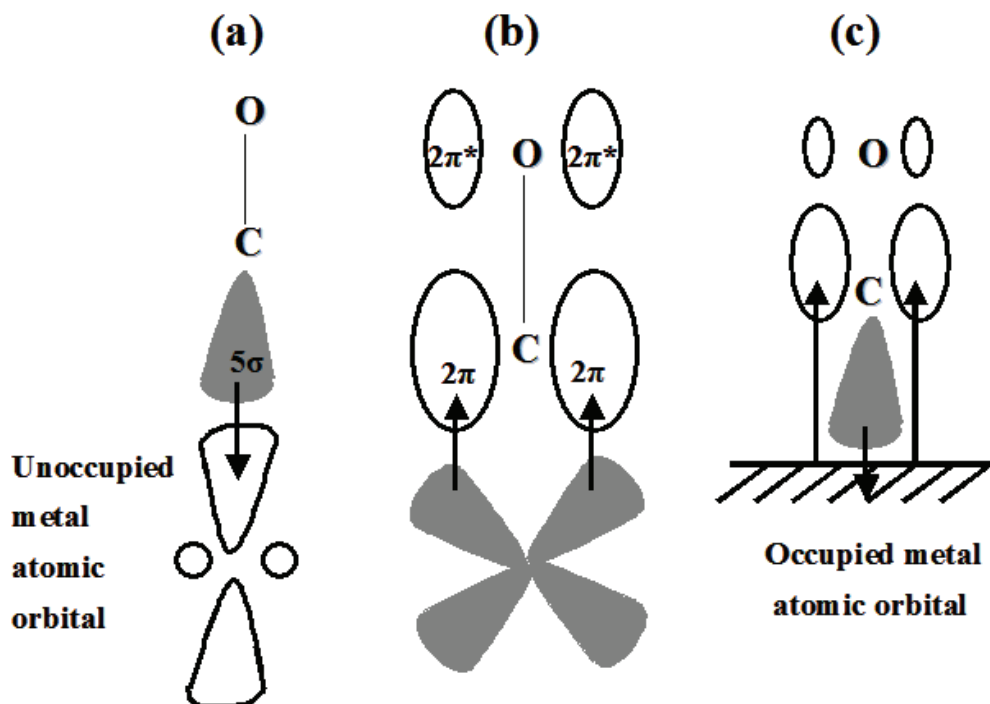
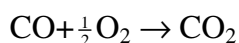


Figure 2.1: A schematic diagram of synergic bonding of CO to a metal. In CO the molecular orbitals are: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^*$. The 4σ orbital is localized on the oxygen atom while the 5σ orbital is localized on the carbon atom and both of these orbitals are non-bonding. The empty $2\pi^*$ antibonding orbital is also available to take parting the interaction with the surface. This combination of σ and π orbitals of CO in the interaction with the surface is called synergic bonding. In the case of molecularly chemisorption of CO, a covalent bond is form by donation of electrons from the 5σ orbital to a vacant metal d orbital (a). At the same time, the full d orbitals are able to donate electron density into the vacant $2\pi^*$ orbitals (b). On adsorption the situation is analogous (c). (adapted after reference [9]).

2.2 CO oxidation over platinum group metals

CO oxidation on platinum group metals surfaces is one of the most widely studied subjects in surface chemistry as a model system of heterogeneously catalysed reactions:



There are several mechanisms that one can imagine for such a reaction on a metal surface, and we will briefly discuss the three most “popular” ones.

Langmuir- Hinshelwood mechanism

Today it is widely accepted that the reaction mechanism for CO oxidation over platinum group metal catalysts follows the so-called Langmuir-Hinshelwood mechanism [10-12], explained in Fig.2.2 a. This mechanism consists of the following steps:

- i) Adsorption of reactant molecules from the gas phase onto the surface.
- ii) Dissociation of molecules on the surface.
- iii) Reaction between adsorbed molecules.
- iv) Desorption of the reaction product(s) to the gas phase.

The assumptions underlying the Langmuir-Hinshelwood mechanism are:

1. The solid surface is uniform and contains a number of equivalent sites each of which may be occupied by at most one adsorbate molecule. The surface itself is not modified by the presence of the molecules and molecules on neighbouring sites do not interact with each other.

2. At each temperature a dynamic equilibrium exists between the gas phase and the adsorbed layer. Adsorbate molecules from the gas phase are continually colliding with the surface. If they impact a vacant adsorption site, they can form a bond with the surface and stick. If they strike a filled site, they are reflected back into the gas phase.

3. Adsorption is random and the adsorbate layer is perfectly mixed. This means for example that no de-mixing (domain formation) occurs of adsorbate molecules in the adsorbate layer.

3. Usually one assumes that the reaction rate is sufficiently low with respect to the impingement rate of reactant molecules that the reaction itself does not modify the equilibrium between reactants and adsorbate layer.

Several refinements have been introduced to this basic form of the L-H mechanism, e.g. allowing the surface to respond (reconstruct and de-reconstruct) to the presence of the adsorbates and allowing the adsorbates to cluster into domains, the reaction then proceeding no longer uniformly over the surface but only at the borders between the domains of different reactants [13-16].

Eley-Rideal mechanism

Another reaction mechanism proposed for catalytic CO oxidation is the Eley-Rideal mechanism [17]. In this mechanism a surface reaction does not involve two adsorbed surface species. If a gas-phase molecule strikes a previously adsorbed molecule there is a possibility that the collision leads to reaction and that the product escapes directly into the gas phase as shown in Fig.2.2 b. Great efforts have been made to prove experimentally that this mechanism occurs [18-19]. Rettner provided the most convincing evidence for an E-R mechanism by investigating the following reactions: $H_{(g)}+D/Cu(111)$ and $D_{(g)}+H/Cu(111)$ [20].

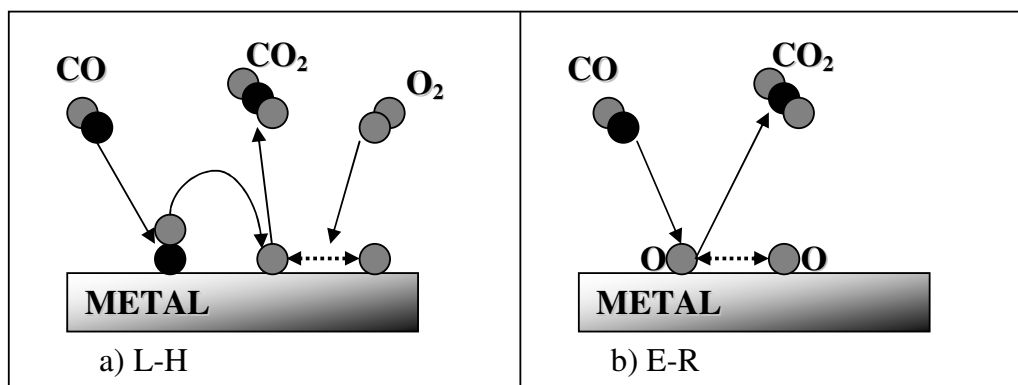


Figure 2.2: Schematic representation of the Langmuir-Hinshelwood mechanism (a) and the Eley-Rideal mechanism (b) for the catalytic oxidation of CO. Dark balls correspond to the carbon atoms and grey balls correspond to the oxygen atoms.

Mars van Krevelen mechanism

In a recent publication, Over and collaborators have proposed an alternative mechanism for CO oxidation over RuO₂ [21]. This mechanism is known as the Mars van Krevelen mechanism (MvK), named after the two scientists, who proposed it in 1954 [22]. Shortly after Over suggestion, Hendriksen and Frenken have provided direct evidence for the Mars van Krevelen mechanism being responsible for the oxidation of CO over the (110) orientation of platinum at atmospheric pressure [23]. In later publications the same authors showed that the MvK mechanism is also active in the CO oxidation over the (100) surface of palladium [24]. In short, the characteristic feature of the MvK mechanism is that some products of the reaction leave the solid catalysts' surface with one or more constituents of the catalysts' lattice. In other words, the catalyst participates more actively in the reaction, playing the role of an intermediate product rather than merely a suitable substrate. The MvK mechanism consists of the following steps (Fig.2.3). First in an oxygen-rich environment, i.e. at a high partial pressure of O₂, and at elevated temperatures, the metal will oxidize. Depending on the detailed energetics of the metal and the oxide, either a thin film forms, as has been found for Pt(110) [25], or the oxidation slowly proceeds further into the metal, as seems to be the case for Pd(100) [26]. After the palladium oxide has been formed at the surface, CO molecules adsorbed on the oxide from the gas phase will react with oxygen atoms from the oxide to produce CO₂. The resulting oxygen vacancies are refilled rapidly by oxygen from the gas phase. In the STM observations by Hendriksen *et al.*, it was observed that during the MvK reaction roughness is formed as a 'by-product' of the reaction [23]. This is ascribed to the fact that each oxygen vacancy renders several palladium atoms temporarily under-coordinated, which introduces a small probability for them to diffuse out of

their original position in the oxide, leaving behind pits in the surface and forming new protrusions on top.

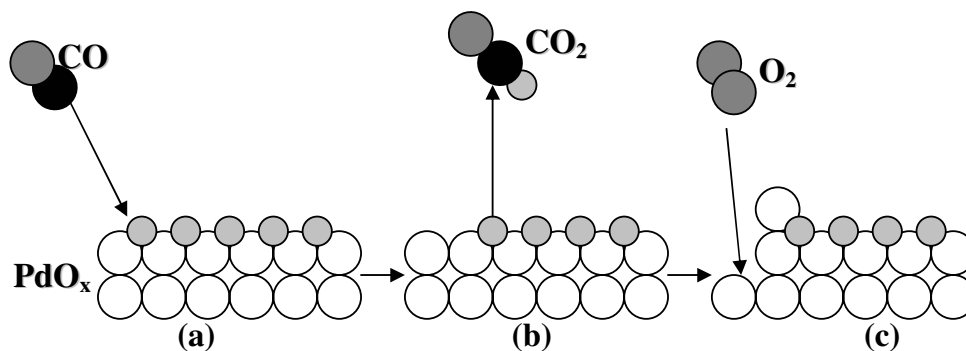
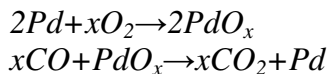


Figure 2.3: Schematic representations of the Mars Van Krevelen mechanism. The empty balls represent Pd atoms. Small grey balls represent the oxygen atoms from the palladium oxide, the dark balls correspond to the carbon atoms and the regular-sized grey balls correspond to the oxygen atoms from gas phase. (a) PdO_x and a CO molecule diffusing to the surface. (b) Reaction between the CO molecule and one oxygen atom from the palladium oxide, the formation of the CO₂ molecule and its diffusion in the gas phase. (c) The diffusion of the left uncoordinated Pd atom and the refill of the vacancy left by the oxygen atom, with oxygen from the gas phase.

2.3 Oscillatory CO oxidation over platinum group metals

One of the most fascinating aspects of chemical reactions taking place under conditions far from equilibrium is the possibility to exhibit instabilities and oscillations. Two key features are used to describe such phenomena: “nonlinearity” and “feedback”. If the first term is related to the mathematics behind these processes, the feedback arises when the products of later steps in the mechanism influence the rate of some of the earlier reactions steps (and, hence, the rate of their own production). This may take the form either of positive feedback (self-acceleration) or negative feedback (self-inhibition) [27]. Another phenomenon closely related to self-sustained oscillations is that of multiplicity of stationary states. In other words under constant external conditions the reaction has more than one stationary state compositions to choose from. A well-known example in heterogeneous catalysis is the oscillating oxidation of CO on platinum group metals (mainly Pt and Pd). As mentioned previously in this chapter, CO oxidation over Pd surfaces is thought to follow Langmuir-Hinshelwood kinetics, similar to the same reaction on other platinum group metals [2]. The kinetics

of a reaction that follows the Langmuir-Hinshelwood can be visualized quite well in a plot of the reaction rate r_{CO} vs. p_{CO} , which is sketched in figure 2.4. At low CO pressure adsorbed oxygen atoms predominantly cover the surface. In this range nearly every CO molecule that strikes the surface is adsorbed and rapidly consumed by reacting with neighbouring adsorbed oxygen atoms and the rate increases linearly with P_{CO} [8]. The rate is limited by CO adsorption in this range. With increasing P_{CO} the concentration of adsorbed CO molecules increases and begins to inhibit the adsorption of oxygen. The rate of CO_2 production passes through a maximum when the coverages of CO molecules and oxygen atoms, θ_{CO} and θ_O are equal and it decreases due to progressive inhibition of O_2 adsorption with further increase of CO pressure. The existence of high and low rate branches of the reaction can be associated with the asymmetric inhibition of the reaction by the two adsorbates. In this case CO forms a densely packed layer upon which O_2 cannot dissociatively adsorb. Conversely oxygen atoms form an open adlayer into which CO readily adsorbs. Therefore, the reaction is poisoned only by high coverages of CO and the reaction rate exhibits two branches. It is not the aim of this section to describe the mathematical modelling of the LH kinetics, but for a better understanding of fig.2.4 few notions must be introduced. It is generally accepted that the temporal evolution of a system can be described by a couple of differential equations:

$$\frac{dx_i}{dt} = F_i(x_i, \mu) \quad (2.1)$$

where F_i contains the kinetics of species (i) and μ is a vector representing the parameters of the system such as pressure, temperature, etc. The dynamical behaviour of the system is usually represented by a trajectory moving in an n -dimensional phase space where the concentrations of the n species X_1, \dots, X_n denote the axes. For simplicity we will just refer to two-dimensional systems [28]. The solutions of the differential equations in this case are called stationary solutions, equilibrium points, steady state points, rest points or fixed points [29]. The term bifurcation denotes a qualitative change in the character of the solution as a parameter is varied such as, for example, a transition from a stable steady state to oscillatory behaviour. The simplest type of the bifurcation that can occur in a dynamical system is from monostability to bistability. This transition is known as the saddle-node bifurcation. In the monostable system all the trajectories converge to a single fixed point that represents the stable stationary state of the system. As the bifurcation parameter μ (pressure, temperature, etc.) is varied, a second stable node may be created so that two stable stationary states coexist, the system has become bistable. Together with the second stable node a third fixed point is created which is called a saddle point. If the stable node attracts the vector flow in all directions, a saddle point is characterized by

having an attractive as well as a repellent direction. If the appropriate feedback exists in a system with bistability of stationary states that link the two states, the system will start to oscillate. All this theory is illustrated in fig. 2.4 where the filled squares correspond to the two stable nodes, while the open squares correspond to the saddle points [27-29].

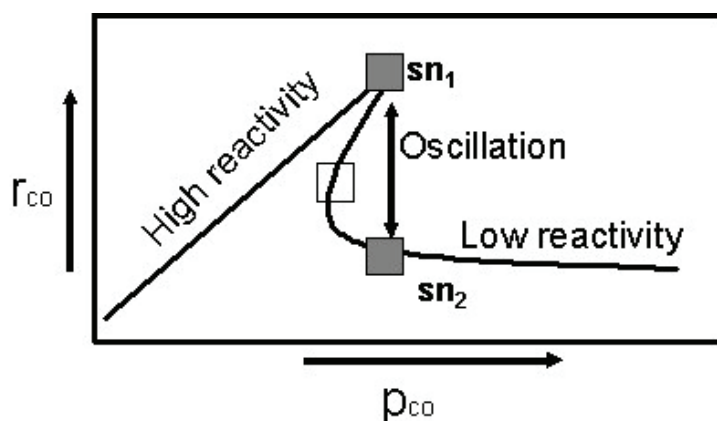


Figure 2.4: The CO oxidation rate on a platinum group metal surface as a function of P_{CO} . Two branches of the reaction rate exist (adapted from ref. [28]).

To summarize, under the steady flow of reactants the reaction rate exhibits three different reactive regimes. These are a *high reactivity* branch, a *low reactivity* branch and a *transition region* connecting the two branches. In the transition region, under specific reaction conditions, oscillations can occur when an additional feedback process is active.

2.4 Summary

In this Chapter we have tried to give a short review of the terms used in the literature to describe CO oxidation on platinum group metals. We have discussed the CO bonding to these metals, the existent mechanism in literature proposed in the literature for the catalytic CO oxidation on these metals and the oscillatory behaviour of such catalytic systems.

2.5 References

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