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# Catalytic CO oxidation on a dysprosium-promoted Pt(1 1 1) surface

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## Abstract

The catalytic CO oxidation reaction has been studied on a dysprosium precovered Pt(1 1 1) single-crystal surface in UHV (partial pressures of reactants up to  $10^{-5}$  Torr range) using mass-spectrometry. The experiments show that the CO oxidation reaction proceeds effectively on the Pt(1 1 1) surface in the presence of a submonolayer of coadsorbed Dy (0.05–0.15 ML) retaining its bistable behavior known for the promoter-free Pt(1 1 1). Coadsorption of Dy leads to a remarkable shift of the reactive phase diagram (bifurcation diagram) towards higher CO pressures. An increase in the Dy coverage leads to a progressing decrease in the reaction rate, the transitions between the reactive and inactive states then become diffuse, the hysteresis collapses and at  $\theta_{Dy} \approx 0.75$  the reaction becomes practically damped. The results are discussed in terms of redistribution of the electron density near the surface induced by the coadsorption of Dy that influences the sticking coefficient of oxygen, binding energy of reacting particles and their interaction on the substrate surface. © 2001 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Electropositive adsorbates such as alkaline earth metals are increasingly used as additives to the automotive three-way catalysts to improve their durability and to supplement the activity of the noble metal components [1]. Recently, e.g. a

barium-compound has been added to the palladium three-way- and NO<sub>x</sub>-SR- (storage reduction) automotive catalysts [2,3]. Despite the practical use the effect of such additives on the catalytic activity of the catalysts are not clear yet.

A recent modification of the reactive phase diagram (bifurcation diagram) for the catalytic CO oxidation using preadsorption of alkali (Li) submonolayers has also demonstrated a principal possibility for fine control of the effective parameter range of this reaction with electropositive coadsorbates [4,5]. Such a parameter range tuning is important e.g. in view of the  $\lambda$ -window problem in

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developing effective automotive catalysts [6]. However, the microscopic mechanism of this alkali-effect is not yet understood, thus it would be of interest to use other electropositive coadsorbates e.g. rare earth metals, which create a similar redistribution of the electron density near the metal surface [7–9]. It is generally known that such a redistribution associated with the alkali and alkali earth coadsorption is mainly responsible for the modification of the kinetics of oxygen adsorption [10] and for a facilitation of the dissociation of oxygen [11], both important steps in the catalytic CO oxidation. An additional motivation for the use of rare earth metals is that they can also provide a higher thermostability of the adsorption system in comparison to the alkali and alkali earth metals [7,12]. We study the CO oxidation on the dysprosium-promoted Pt(1 1 1) single-crystal surface.

The choice of the Pt(1 1 1) surface as a substrate for our study of Dy-modified CO oxidation is mainly due to the fact that the reaction has been studied comprehensively on this surface, the previous experimental and theoretical work is thoroughly summarized in the review by Zhdanov and Kasemo [13] and in the recent article by Berdau et al. [14]. The main result of the previous studies is that the CO + O<sub>2</sub>/Pt(1 1 1) system does not show in UHV the spatiotemporal oscillations usually observed for other, crystallographically open Pt surfaces [15,16]. The reaction system only shows two stable steady states, a state of high reactivity (oxygen covered surface) and of low reactivity (CO covered surface), separated by the region of bistability where a hysteresis is observed upon the cycle-wise varying external parameters, e.g. partial CO pressure [14]. This relatively simple behavior can be theoretically modeled employing a Langmuir-Hinshelwood (LH) reaction mechanism [16] which assumes coadsorption of both oxygen and CO during the reaction. The corresponding modeling e.g. using the Monte-Carlo method within framework of the Ziff-Gulary-Barshad (ZGB, [17]) model has been performed for the promoter-free [13] as well as for the alkali-precovered (with Li, [5]) surface, revealing basic features of the reaction behavior and thus promising hope for understanding the role of Dy as an additive in this reaction.

## 2. Experimental

Experiments were carried out in a 20 l stainless steel UHV-chamber with a background pressure of about  $2 \times 10^{-10}$  Torr, which was used as a gradient free continuous flow reactor. The CO gas was obtained by the  $\text{CaCO}_3 + \text{Zn}(750\text{C}) \rightarrow \text{CaO} + \text{ZnO} + \text{CO}$  reaction and O<sub>2</sub> gas by thermal decomposition of KMnO<sub>4</sub>, respectively. After further purification gases were stored in separate reservoirs and admitted in a controlled way into the reactor. The partial pressure of O<sub>2</sub> was measured by means of a Bayard-Alpert-type ion gauge. The CO pressure was calibrated before the experiments and monitored in the course of experiment using a mass spectrometer. The design of the sample holder allowed the 3D-movement and rotation of Pt- and Mo-sample (used for calibration of the Dy-source) as well as the sample heating up to 1600 K, measured with a W-W/Re thermocouple. The platinum sample (effective area  $\sim 40\text{ mm}^2$ ) was X-ray oriented and cut with an accuracy higher than  $0.5^\circ$  from a high purity single-crystal rod. For the cleaning of the Pt-surface standard procedures as described elsewhere were employed [14,18]. The Dy source was prepared by vacuum melting of pure Dy-metal in a tantalum crucible [19] and the purity of the Dy atomic beam has been controlled with a mass spectrometer. The Dy beam intensity was calibrated by measurements of the work function of the Mo(1 1 2) surface (second sample mounted on the holder) whose coverage dependence is known from independent LEED measurements [20]. Thus the Dy coverage on the Pt(1 1 1) surface (defined as  $\theta_{\text{Dy}} = n_{\text{Dy}}/n_{\text{Pt}(1\ 1\ 1)}$ , where  $n_{\text{Dy}}$  and  $n_{\text{Pt}(1\ 1\ 1)}$  are corresponding concentrations of Dy adatoms and Pt surface atoms, respectively,  $n_{\text{Pt}(1\ 1\ 1)} = 1.5 \times 10^{15}\text{ cm}^{-2}$ ), could be easily evaluated from the time of Dy-deposition. The reaction rate was evaluated mass spectrometrically as a CO<sub>2</sub> production rate.

## 3. Results and discussion

As already noted, the CO oxidation reaction on the promoter-free Pt(1 1 1) surface has comprehensively been studied experimentally using the

photoelectron emission microscope (PEEM) and mass-spectrometry methods [13,14]. The absence of spatiotemporal oscillations, at reactant pressures up to  $10^{-5}$  Torr (kinetic oscillations in this reaction on Pt(111), recently observed at higher oxygen pressures are related to the oxidation of the Pt surface itself [21]) and the existence of the region of bistability between two stable states, of the high and of the low reactivity correspondingly are main results of those studies. Experimentally, one observes a hysteresis at transitions from the CO covered state (low reactivity) to the oxygen-covered and vice versa (high reactivity) with a width that depends to some extent on the parameter-scan rate [13,14]. It was shown in Ref. [14] that one deals in this case with a true region of bistability which would also exist in the case of an infinitely slow scan rate, therefore we do not consider this aspect in the present study.

The first aim of our experiments was to prove the influence of preadsorbed Dy on the bistable reaction behavior. Fig. 1a exhibits the reaction rate ( $\text{CO}_2$  production rate) upon a cyclic variation of the CO partial pressure at constant substrate temperature (470 K) and constant  $\text{O}_2$  partial pressure ( $6 \times 10^{-5}$  Torr) at different Dy coverages (0.05–0.4 ML). Fig. 1b shows analogous results obtained at a lower temperature (415 K) and a somewhat lower ( $1.5 \times 10^{-5}$  Torr) oxygen pressure. One observes for all experimental conditions that the reaction system keeps its main property characteristic for the promoter-free surface, namely: two monostable regions (of high and of low reactivity correspondingly) which are separated by a region of bistability (characterized by a pronounced hysteresis). On the high reactivity “side” an increase in the partial CO pressure causes an almost linear increase in the reaction rate until the surface becomes covered at transition point  $p_{\text{CO}} = \tau_A$  by a more or less dense layer of CO. This inhibits the dissociative oxygen adsorption (two adjacent adsorption sites are always required per one oxygen molecule) and causes a transition to the low reactivity state, where the system remains even if the CO partial pressure is now reduced again, until transition point  $p_{\text{CO}} = \tau_B$  is reached. As one sees in Figs. 1a and b an increasing Dy coverage suppresses the reaction progressively: the reaction rate

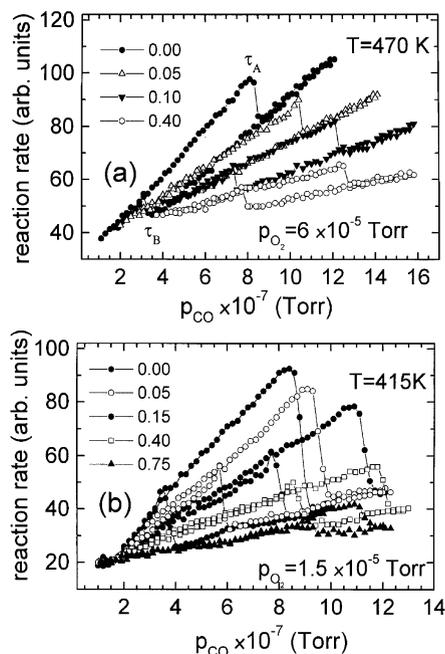


Fig. 1. (a) Hysteresis in the reaction rate ( $\text{CO}_2$  production rate) as measured mass spectrometrically upon cyclic variation of the CO partial pressure for constant substrate temperature (470 K) and constant  $\text{O}_2$  partial pressure ( $6 \times 10^{-5}$  Torr) at different Dy coverages (0.05–0.4 ML). Transition points  $\tau_A$  from the oxygen-covered state (high reactivity) to the CO-covered state (low reactivity) and vice versa ( $\tau_B$ ) are marked. (b) the same as in (a) but for  $T = 415$  K and  $\text{O}_2$  partial pressure of  $1.5 \times 10^{-5}$  Torr. The reaction still proceeds effectively at submonolayer ( $\theta_{\text{Dy}} \leq 0.1$ ) coverages, increase of Dy coverages damps the reaction progressively.

of  $\text{CO}_2$  formation always decreases when the Dy coverage increases, the transitions between the reactive and inactive states then become diffuse and the hysteresis collapses. The coadsorbate coverage  $\theta_{\text{Dy}} = 0.75$  practically damps the  $\text{CO}_2$  formation. Nevertheless, the results presented in Figs. 1a and b demonstrate that the bistable region still exists in a wide range of surface concentrations of preadsorbed Dy and at coverages  $\theta_{\text{Dy}} \leq 0.1$  the reaction rate itself is only slightly affected. The physical reason for this is the competition of the increase of the sticking coefficient for oxygen caused by an electropositive coadsorbate and the reduction of the number of available adsorption sites also taking place in the case of alkali coadsorption [5]. At very

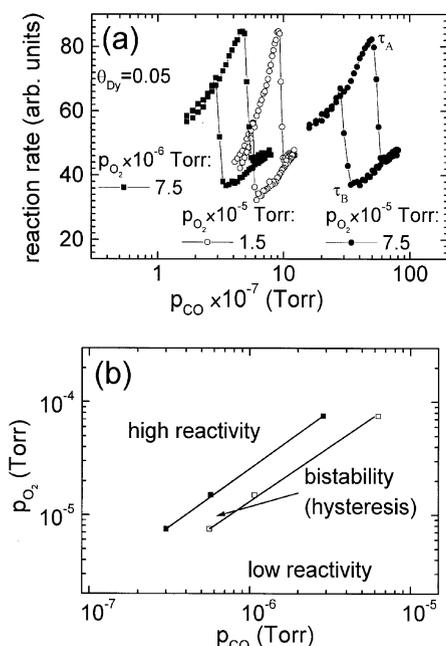


Fig. 2. (a) Set of hysteresis loops measured at  $T = 470$  K, constant Dy coverage ( $\theta_{Dy} = 0.05$ ) for different  $p_{O_2}$  pressures ( $7.5 \times 10^{-6}$ – $7.5 \times 10^{-5}$  Torr). Similarly to the promoter-free Pt(111) surface an increase in  $O_2$  pressure causes the shift of bistable region toward higher CO pressures. (b) An isothermal reactive phase diagram constructed using the transition points from the hysteresis loops shown in (a). Boundary lines are the phase separation lines.

low submonolayer coverages the dipole moments of Dy adatoms modify remarkably the surface potential, thus influencing the kinetics of oxygen adsorption, but reducing only slightly the effective area of the catalytically active surface. In this case, one expects a shift of the maximum of the  $CO_2$  formation to higher CO pressures. Such an effect can be conveniently demonstrated in the reactive (kinetic) phase diagram (bifurcation diagram) that relates the behavior of the system to state parameters ( $p_{O_2}$ ,  $p_{CO}$ ,  $T$ , etc.). The term *phase diagram* is used in analogy to equilibrium thermodynamics as proposed by Schlögl [22,23]. The simplest example of such a diagram can be constructed from measurements of a set of hysteresis plots at constant substrate temperature for different  $p_{O_2}$  pressures. Fig. 2a exhibits such a set measured at  $T = 470$  K, constant Dy coverage ( $\theta_{Dy} = 0.05$ ) for

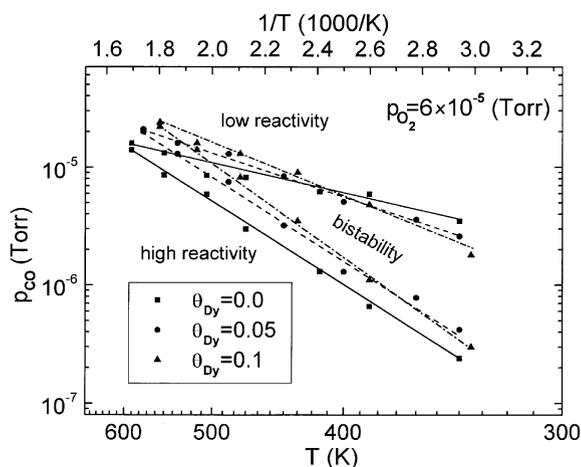


Fig. 3. Reactive phase diagram for the CO oxidation on the promoter-free (solid lines) and for the Dy-promoted Pt(111) surface (0.05 and 0.1 ML) at constant oxygen pressure  $6 \times 10^{-5}$  Torr. Already very small (0.05 ML) Dy-coverage causes an observable shift of the reactive region to higher CO pressures.

different  $p_{O_2}$  pressures ( $7.5 \times 10^{-6}$ – $7.5 \times 10^{-5}$  Torr). Similarly to the promoter-free Pt(111) surface an increase in  $O_2$  pressure causes a shift of the bistable region to higher CO pressures.

By measuring such sets at varying parameters one obtains the “transition points” from the oxygen-covered state (high reactivity) to the CO-covered state (low reactivity) and vice versa, which form the “phase boundaries” separating the bistable region from the two monostable regions. Such boundary lines presented in  $\log(p_{O_2})$ ;  $\log(p_{CO})$  coordinates compose an isothermal phase diagram shown in Fig. 2b displaying two parallel phase separation lines, as known from PEEM measurements for a promoter-free Pt(111) surface [14]. It is clear that the present number of the experimental points in the diagram permits only a qualitative view into the reaction kinetics, but the main property, namely, the existence of the bistability region in a wide range of the partial oxygen pressure remains also in the presence of Dy submonolayer.

A better insight into the reaction behavior can be obtained by a diagram measured at constant  $O_2$  pressure and at varying CO partial pressure and temperature. Corresponding phase boundaries are displayed in Fig 3 in  $p_{CO}$ ,  $1/T$  coordinates (the

usual temperature scale is also shown for convenience) for a clean (Dy-free) and Dy-precovered ( $\theta_{\text{Dy}} = 0.05$  and  $0.1$ ) surface. Hysteresis has been observed in a wide range of temperatures. It is narrowing with increasing temperature and disappears (cusp point, or critical point in analogy to equilibrium systems [24]) for a clean Pt surface at about 590 K.

For the Dy-precovered surface, a clear shift of the diagram to higher CO pressures is observed in the temperature range  $415 \leq T \leq 555$  K, as previously observed for coadsorbed Li [4,5]. The effect of preadsorbed Dy becomes also apparent in a decreasing cusp point temperature (where the bistable region vanishes): for  $\theta_{\text{Dy}} = 0.05$  it is estimated to be at about 575 K and at  $\theta_{\text{Dy}} = 0.1$  at 555 K, correspondingly. The reason for the shift to higher CO pressures seems to lie mainly in the Dy-caused modification of the sticking coefficient of oxygen, which influences the competitive CO and oxygen coadsorption at reaction conditions, also taking place in the case of an alkali-modified reaction [4, 5]. Modifications of the binding energy of reactive adsorbates (especially that of oxygen) and of the CO–O interaction induced by a coadsorption of an electropositive coadsorbate can also take place as suggested by studies of Dy adsorption on initially oxidized metal surfaces [25] and by recent theoretical considerations of the CO–O interaction in the presence of metal coadsorbates [26]. These possible mechanisms contribute less to the general effect since it is known, that modification of the electron density near the surface by an externally applied electrostatic field already causes a comparable shift of the reactive phase diagram [27]. Nevertheless, an additional investigation of the role of the coadsorbed Dy in modifications of the adsorption energetics of CO and oxygen as well as a detailed experimental study of the kinetics of the oxygen- and CO-adsorption on Pt in the presence of Dy, seem to be necessary for a further progress in understanding the role of rare earth metal additives in the CO oxidation reaction.

#### 4. Conclusions

The catalytic CO oxidation reaction has been studied on a dysprosium precovered Pt(111)

surface using mass-spectrometry. The experiments show that the CO oxidation reaction proceeds effectively on the Pt(111) surface in the presence of a submonolayer of coadsorbed Dy (0.05–0.15 ML) retaining its bistable behavior known for promoter-free Pt(111). Coadsorption of Dy leads to a remarkable shift of the reactive phase diagram ( $p_{\text{CO}}, 1/T$ ) to higher CO pressures, primarily due to a modification of the sticking coefficient of oxygen, caused by the Dy-induced redistribution of the electron density near the surface. This effect is basically similar to the one recently observed for the Li-promoted Pt surface. Increasing the Dy coverage (to 0.75 ML) leads to a significant decrease in the reaction rate, mainly due to the occupation of the active adsorption sites by Dy adatoms in analogy to the role of coadsorbed alkali in this reaction. The transitions between the reactive and inactive states then become diffuse and the hysteresis collapses.

The reaction behavior at submonolayer Dy coverages indicates that the use of small amounts of rare earth metals as additives promises to allow a fine tuning of effective range of the control parameters in the CO-oxidation on Pt-based catalysts.

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