



Generation of surface steps on Pt(977) induced by the catalytic oxidation of CO



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ABSTRACT

The catalytic oxidation of CO has been investigated on the stepped Pt(977) surface at near ambient pressure and elevated temperature. It has been found that the reactivity is maximum at approximately the stoichiometric proportion of reactants and that surface monoatomic steps are generated by the reaction itself, being most abundant when the reaction proceeds with maximum efficiency.

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1. Introduction

Atoms at surface steps have lower atomic coordination than regular surface atoms in flat terraces, and already in 1925 [1], they were proposed as possible active sites in surface chemical processes. The early papers from the Somorjai group [2] suggested that surface steps in Pt surfaces were active sites for C–C and C–H bond breaking. Further published literature provides a variety of examples of dissociation of molecules chemisorbed at step sites. To mention some, Xu et al. [3] observed with Infrared (IR) techniques that on Pt(335), dissociative adsorption of O₂ and CO occurred preferentially on the step sites. Zambelli et al. [4] demonstrated with STM that the dissociation of NO on Ru(0001) occurred at steps. Dahl et al. [5] reported from adsorption rate measurements and density functional calculations that the dissociation of N₂ on Ru(0001) occurs at the steps with much higher probability than on terraces. Also, IR measurements by Zubkov et al. [6] evidenced the dissociation of CO on Ru(109) steps, and Vang et al. [7] evidenced with STM measurements and calculations that steps are more efficient for C–C bond breaking than for C–H bond breaking when ethylene is adsorbed on Ni(111). The above examples illustrate that steps play a key role on the dissociative

chemisorption of gas molecules. In most cases, the experimental support arises from UHV surface techniques.

Surface chemical reactions are intrinsically more complex than chemisorption processes since they involve additional elementary steps. This additional complexity blurs the precise role of steps in many cases. The intuitive idea that the presence of steps always increases the reactivity can be questioned. This is technically difficult to address since only a few techniques can provide direct structural information under reaction conditions. Already in the initial papers from the Somorjai group on the dehydrogenization of cyclohexane on stepped Pt surfaces, the authors observed that the maximum turnover frequency (TOF) did not occur on the surface with the highest density of steps [8]. Gland et al. [9] investigated under UHV the oxidation of CO on Pt(321) and concluded that atomic oxygen reacts with the CO adsorbed on the terraces more rapidly than with CO adsorbed on the steps. Ford et al. [10] investigated with thermal desorption spectroscopy, the adsorption of a variety of gases on several stepped surfaces and their generally concluded that their results did not support the ideas that surface steps and kinks have any effect on catalytic activity. Szabo et al. showed that CO adsorbed on the terraces was more effective in producing CO₂ than CO on the steps [11]. The same ideas were investigated in Pt nanoparticles supported on alumina by Atalik and Uner [12], which studied the oxidation of CO under UHV conditions and concluded that atoms at flat surfaces had higher activity per surface site than low coordinated edge or corner atoms. Experiments at atmospheric pressure by Silvestre-Albero et al. [13] on supported

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Pd catalysts on a hydrogenation reaction gave similar results. The reaction was found to be particle size independent for particles larger than, 4 nm which exhibit TOFs identical to Pd(111) single crystals. Similar results reported by Goodman [14] on the oxidation of CO at a pressure of a few torr on Pd nanoparticles did not reveal noticeable dependence of the CO₂ formation rate on the Pd cluster size. However, Au particles seem to be an exception since the results are opposite. As shown by Lopez et al. [15], low coordinated Au atoms were associated with high TOFs since small Au particles (2–4 nm) exhibited TOFs ~100 times larger than particles of 20–30 nm in size. Most published studies deal with the variation in the reaction rate for different densities of steps; however, the variation in the step density during the reaction has been much less investigated.

A previous paper by Hendriksen et al. [16] on the oxidation of CO to CO₂ on Pd(001) surfaces exposed to 500 mbar of O₂ and 25 mbar of CO investigated with surface X-ray diffraction *in operando* conditions, evidenced an oscillatory reaction rate and surface morphology. The surface was periodically changing from metallic to oxidized, and the production of CO₂ was also oscillating in phase with the structure of the surface. High reaction rates corresponded to oxide surfaces and low rates to metallic surfaces. The high reaction rate was associated with a broadening of the diffracted peaks indicating an increase in surface roughness that was interpreted as being due to an increase in the density of surface steps. From these observations, it was concluded that surface steps had a key role on the reactivity.

We report here new results on *in situ* CO oxidation experiments near atmospheric pressure on a vicinal Pt(977) surface, which consists of a periodic array of equally separated monatomic steps, where we have identified the role of the steps on the reaction rate not by measuring the evolution of the width of the diffracted peaks from the surface lattice as previously, but by monitoring the evolution of the intensities of the diffracted peaks arising from the step array itself. In our experiments, the partial pressures of CO and O₂ during the reaction were always kept outside of the self-sustained oscillatory regime described in Ref. [16].

In a few words, we found that the actual surface under reaction conditions is faceted and consists of (111) and (977) areas that have to coexist with rough or step bunched areas to keep the mean surface orientation. The maximum density of (977) areas and hence of atomic steps occurred when the reactants had the stoichiometric proportion (two COs per one O₂ molecule). Excess of CO or O₂ over the 2:1 nominal ratio in the gas mixture caused an increase in the proportion of (111) facets and a decrease in (977) revealing the disappearance of some monoatomic steps. If the gas proportion was returned back to the stoichiometric ratio, the (977) facet increased, i.e., steps were regenerated. This process was reversible.

In short, the reaction drives the morphology of the catalyst optimizing the density of monoatomic steps to maximize the rate.

2. Materials and methods

The Pt(977) sample was a disk of diameter 10 mm and thickness 3 mm obtained after cutting a single crystalline rod. Previous to the experiment, it was annealed to 1000 °C in air to recrystallize and to eliminate carbon impurities. Afterward, it was mounted on a thermally insulated ceramic heater which allowed reaching temperatures up to 900 °C as measured with a thermocouple in contact with the crystal. The crystal and heater were installed in a flow reactor previously described [17] connected to a UHV chamber allowing sputtering/annealing cycles for surface preparation. The reactants, CO and O₂, were introduced with a computer controlled gas manifold which allowed to precisely define their relative proportions. The partial flows were set at the entrance of the reactor,

whereas the total pressure P in the reactor, in the range 10–200 mbar, was set by a pressure controller at the exit. In this way, the ratio of the partial pressures of the reactants $R = P_{\text{CO}}/P_{\text{O}_2}$ was determined and used as an experimental variable to describe the reaction conditions. $R = 2$ corresponds to the stoichiometric proportions of the reactants whereas $R > 2$ and $R < 2$ to CO and O₂ rich conditions, respectively. A leak from the reactor to a gas analyzer in the UHV chamber allowed monitoring the production of CO₂.

Concerning the reactivity of the sample, after it was mounted on the ceramic heater, the vacuum system was pumped down and baked to reach UHV pressures. This resulted in a contaminated sample that was inert and did not produce CO₂. To prepare a clean and reactive surface, we sputtered the front face of the crystal (the 977 face) with Ar ions, and later, we annealed the crystal to order the surface lattice. During ion sputtering, a fraction of the ion beam impinged on one side of the crystal, and from the total sputtered surface area, about 14% corresponded to the edge of the crystal which might contribute to the reactivity. In our analysis, this edge effect has been ignored. In addition, we have assumed that the back side of the crystal was unreactive since it was in close contact with the ceramic heater. Also, in previous experiments, the reactivities of the vessel, sample holder, and heater were measured and found to be negligible.

The turnover frequencies have been estimated with two methods: measuring the partial pressure of the produced CO₂ and measuring the temperature increase in the sample due to the exothermic heat of reaction with the appropriate calibration of the thermal characteristics of the sample heater. The sample was near adiabatic conditions due to the isolating sample heater. Within a factor two to three, both methods agreed which is considered acceptable due several experimental uncertainties.

The reactor chamber was installed on a diffractometer at the Surface Diffraction beamline (ID3) at ESRF [18]. Seventeen keV X-rays passing through the Be dome of the reactor impinged the crystal surface at a grazing angle of 1–2°. Diffracted intensities were collected with a 2D maxipix pixel detector from ESRF while rotating the sample as required to sweep the reciprocal space. We described the fcc crystal lattice with an orthogonal basis adapted to our vicinal surface: $A = (-7, 9/2, 9/2)a_0$, $B = (0, -1/2, 1/2)a_0$, $C = (9, 7, 7)a_0$, $\alpha = \beta = \gamma = 90^\circ$, $a_0 = 0.3924$ nm (see Fig. 1a). The corresponding H, K, L coordinates are used to index reflections in reciprocal space. As an example, the (111) reflection in conventional reciprocal units has $(H, K, L) = (0, 2, 23)$. In this basis, the diffuse lines of diffracted intensity perpendicular to the surface and parallel to the L axis in reciprocal space which are designed as crystal truncation rods (CTR) [19] have even values of $H + K$.

Fig. 1 panel a illustrates the definitions of the vectors **A** and **C** and a schematic drawing of the stepped surface. Panel b shows a portion of the H – L plane (at $K = 0$) of reciprocal space and the corresponding diffracted intensities. In addition to the Bragg reflections from the bulk of the crystal which have the largest intensities, the diffuse streaks (CTRs) of intensity emanating from the Bragg reflections and parallel to the L axis are evident. They are fingerprints of the 977 plane at the surface. The inclined streak of intensity in the figure arises from 111 surface facets. The coexistence of stepped and 111 surface areas was also reported previously on Pt(997) and attributed to trace impurities or intrinsic thermal instability [20].

3. Results and discussion

Setting $P = 200$ mbar and the stoichiometric proportions of the reactants ($P_{\text{CO}}/P_{\text{O}_2} = 2/1$) which corresponds to $R = 2$, while heating the sample from room temperature to 200 °C did not produce any

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