



High-pressure *operando* STM studies giving insight in CO oxidation and NO reduction over Pt(1 1 0)



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ABSTRACT

Two catalytic systems have been studied at high pressures on the Pt(1 1 0) surface on an atomic level. The first system was the oxidation of CO by O₂ towards CO₂. In the framework of the second reaction, namely NO reduction, the effect of room temperature exposure of the surface to NO and H₂ was investigated. To study these reaction systems at relevant pressures, the ReactorSTM has been used. This is a unique system which consists of a compact STM in which a flow reactor is integrated. The combined reactor with STM is housed inside a conventional vacuum system to allow for traditional surface science preparation and analysis techniques. The STM images obtained with the ReactorSTM under reaction conditions show the lifting of the (1x2) missing row reconstruction by high-pressure CO exposure. The lifting is followed by the formation of the (1x1) metallic Pt(1 1 0) structure for high CO/O₂ ratios and a (1x2) lifted-row type surface oxide structure for more O₂-rich conditions. The room temperature exposure of Pt(1 1 0) to H₂ results in the formation of a (1x4) missing-row structure and deeper, nested missing rows. The exposure to high-pressure NO removes these missing-row structures.

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1. Introduction

Much of our current knowledge of the precise mechanisms underlying chemical reactions at catalyst surfaces is derived from experiments under ultra-high vacuum (UHV) or high vacuum (HV) conditions. This discrepancy with respect to the typical working conditions of practical catalysts (*i.e.*, high pressures (HP) and elevated temperatures) comes from the fact that many surface-sensitive techniques such as low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) cannot be combined easily with the environment to which a catalyst would normally be exposed. Typical examples of catalysis would be the three-way catalyst in an automotive exhaust system, or catalytic processes in the petrochemical industry. Moreover, UHV conditions provide a clean and easily controllable environment for accurate experiments [1,2]. Although such low-pressure model studies have contributed extensively to our fundamental understanding of catalysts, recent investigations at high gas pressures have yielded new insights that go beyond the mere extrapolation of the low-pressure results [3–6]. This difference is often referred to as the “pressure gap” [7,8]. Recently, several

surface analysis techniques have been adapted to realistic conditions. Examples are transmission electron microscopy (TEM) [9], surface X-ray diffraction (SXRD) [10], scanning tunneling microscopy (STM) [8,11,12], and atomic force microscopy (AFM) [13].

Scanning tunneling microscopy is one of the few atomically sensitive surface science techniques that do not introduce fundamental problems or limitations when bridging the pressure gap. This technique can operate in the full range from UHV to HP of, *e.g.*, 1 bar and beyond, and from cryogenic temperatures to temperatures well above 1000 K [14,15]. With its capability to image surfaces with atomic resolution, STM holds the promise to determine the detailed dependence of the structure of model catalyst surfaces on various gas environments, to identify the active sites for catalytic reactions, and to elucidate the role of possible promoters, all under the relevant, high-pressure, high-temperature conditions of the catalytic processes of interest. The weak, local interaction of the tip with the surface provides confidence that in most cases this interaction will not significantly affect the structure and the properties of the catalyst. These advantageous properties of the technique go hand-in-hand with a demanding combination of technical difficulties, involving, *e.g.*, the imaging stability of the instrument in terms of drift and noise resulting from temperature and pressure variations, and from the presence of a gas flow. In addition, the signal-to-noise ratio in the detection of the reaction products in the gas mixture is demanding as well.

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In order to investigate the relationship between surface structure and activity of a catalyst under industrially relevant conditions, we have developed the ReactorSTM system [16]. This system combines a small flow reactor, integrated with an STM into a UHV system that is equipped with standard, high-quality surface preparation and analysis techniques, such as ion bombardment, metal deposition, XPS, AES, and LEED. The architecture of the system is such that the sample can be transported from the various sample preparation and analysis tools into the ReactorSTM without breaking the UHV conditions. During the HP STM experiments, the UHV stays uncompromised even at pressures inside the reactor well above 1 bar. The flow-reactor geometry and the special design of the low-volume high-purity gas supply system allows us to continuously control the gas mixture composition in the reactor, the flow rate, and the reactor pressure, and it allows for rapid, time-resolved analysis on the gas effluent from the reactor during STM imaging, without the need to retract the tip, which would result in a 'blind moment'. In this way, this system enables us to study the surface structure of an active catalyst with atomic resolution, combined with simultaneous reactivity measurements. Thereby, we can directly correlate structural changes with chemical activity. The system is a strongly improved version of the prototype that we reported on earlier [3,11] and a commercial version has been developed by Leiden Probe Microscopy BV [17]. In this paper, we report on the first results from this new instrument applied to two different catalytic reactions, both on the Pt(1 1 0) surface: CO oxidation and NO reduction. CO oxidation is one of the reactions occurring in the catalytic cleaning of exhaust gases from automotive engines. Selective oxidation of CO to CO₂ has also received major attention in order to clean H₂ streams for fuel cells [18]. Typical catalysts used for this reaction include the noble metals, such as Pt [19]. The (1 1 0) surface of Pt is perhaps the best studied surface after Pt(1 1 1) for the oxidation of CO. Early studies of this reaction system have revealed highly interesting phenomena, such as, kinetic oscillations [20] and reaction induced faceting [21]. However, these phenomena were observed in a pressure range from high vacuum to UHV and using traditional surface science techniques. This experimental window in which detailed information of the surface can be obtained has been dramatically increased by the recent developments of *in situ* and *operando* techniques. Because of the interesting discoveries obtained in vacuum, it is easy to understand that this surface received much attention from researchers using these newly developed techniques. One of the key questions is whether the behavior observed under vacuum conditions can be extrapolated to real reaction conditions and which new surprises can be found on the other side of the pressure gap.

High-pressure STM [3] and SXRD combined with DFT [4] have revealed the appearance of new surface structures and compositions, depending on the gas composition. Two of these structures are oxidic in nature. One is a surface oxide probably stabilized by carbonate ions and oxygen atoms. This oxide is observed when the ratio between the partial pressures of CO and O₂ is not too low. The other oxidic structure is a thin film of bulk-like α -PtO₂ and is formed at lower CO to O₂ partial-pressure ratios. Interestingly, both oxides show a higher reactivity towards CO oxidation compared to the metallic surface. The formation of α -PtO₂ and the reactivity to CO has been confirmed by one ambient-pressure XPS study [22], while a second study at slightly different pressure and gas compositions compared to the STM and SXRD studies showed only the metallic surface [23]. In addition to the surface oxide observed by SXRD, a different structure has been observed in which O atoms bind to the FCC hollow sites of a reconstructed (1x2)-Pt(1 1 0) surface. In this surface oxide, the O-atom-induced stress leads to the ejection of Pt atoms in a highly ordered manner, so that a Pt(1 1 0)-(12x2)-220 structure is adopted [24]. However, DFT combined with *ab initio*

thermodynamics predicts that this surface oxide is not stable under reaction conditions [25,26].

The oxidation of CO by O₂ serves as a 'model system' to demonstrate the improved resolution of the ReactorSTM under catalytic conditions.

The second part of this work describes experiments on the interaction between NO and H₂ and the Pt(1 1 0) surface. These interactions are key factors in understanding the selective reduction of NO, which is an extremely important process to clean exhaust gases of engines and large turbines. In contrast to the oxidation of CO, there is hardly any *in situ* or *operando* result reported on the reduction of NO. Previous work from our group shows that results obtained under reaction conditions strongly differ from the results obtained in UHV on the reaction between NO and CO on Pt(1 0 0) [27]. On Pt(100), the surface switches between a (1x1) reconstruction and a quasi-hexagonal structure depending on the CO/NO ratio at 1.25 bar.

Different reducing agents can be used for this reaction, such as unburned fuel remains, CO and H₂. Hydrogen can be formed in exhaust gases by a water gas shift reaction (Eq. (1)) or via steam reforming with for example methane (Eq. (2)).



We continue this paper with a brief description of the ReactorSTM and the considerations with respect to purity and contaminations. After the experimental section, the results of the high-pressure, high-temperature study of CO oxidation on Pt(1 1 0) are described and discussed, followed by the structural changes observed on the same surface during high-pressure room temperature exposure to H₂ and NO.

2. Experimental

The results presented in this paper have all been obtained with the ReactorSTM [16] and establish the first scientific output of this unique system, which is an improved version of the HP STM described by Rasmussen et al. [11]. Herbschleb et al. describe the ReactorSTM in full detail elsewhere [16]. Therefore, we only summarize the most important features of the system. The ReactorSTM is a flow cell integrated within an STM inside a UHV system. Only a few parts of the STM are exposed to the reactive gases, *i.e.*, the tip and a slider that forms part of the STM's coarse approach mechanism. Most parts of the STM, such as the piezo tube, are outside the flow cell.

The combination between a UHV system and a flow cell gives the best of both worlds, fundamental surface science and the more applied catalytic research. We can use model catalysts and obtain a very clean and controlled starting point for the high-pressure experiment. Because we use a small flow reactor instead of back-filling a large-volume chamber, we can measure the reactivity with a much lower detection limit and higher time resolution. This reactivity is measured by leaking a small fraction of the gas from the reactor into a separate UHV chamber housing a Quadrupole Mass Spectrometer (QMS).

The Pt(1 1 0) sample, which was spark cut and polished to within 0.1° from the (1 1 0) plane [28], was cleaned with repetitive Ar⁺ sputtering and annealing in UHV at temperatures between 900 and 1100 K before every experiment. This procedure was complemented with an anneal step at 800 K in an oxygen atmosphere (1 × 10⁻⁸ – 1 × 10⁻⁷ mbar) to remove residual carbon. The removal of carbon and other impurities was checked with AES, until the peaks corresponding to impurities were on the level of the noise. In addition to the surface purity, LEED was used to determine the surface structure. The crystal was cleaned until LEED

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