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Insight into a Pressure and Materials Gap: CO Oxidation at "Ruthenium" Catalysts

K. Reuter

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin - Germany
e-mail: reuter@fhi-berlin.mpg.de

Résumé — **Impact de la pression et de l'état du matériau sur la réactivité : oxydation de CO avec des catalyseurs de « ruthénium »** — Des travaux expérimentaux et théoriques récents sur l'oxydation du CO avec des catalyseurs au ruthenium offrent un aperçu fascinant sur les origines microscopiques des « gouffres » des pressions et des matériaux, sujet souvent controversé entres les études réalisées dans des conditions réalistes de pression et celles réalisées sous ultravide (UHV). En se concentrant sur le catalyseur modèle Ru(0001), le système considéré présente en fait deux composants importants relatifs à ce sujet. En premier lieu, un environnement riche en oxygène transforme le matériau Ru en RuO_2. Ainsi, des études antérieures sur la pression ambiante portant sur les catalyseurs au « ruthénium » se concentraient en fait sur un film d'oxyde formé à la surface. En second lieu, même après que le RuO_2 se soit formé, la composition de surface varie fortement selon la pression ; il faut également noter que sur le RuO_2 (110) formé, il y a une phase de surface de basse pression qui est couramment étudiée sous UHV, mais qui présente peu d'éléments en commun avec la situation où le catalyseur est actif.

Abstract — Insight into a Pressure and Materials Gap: CO Oxidation at "Ruthenium" Catalysts — *Recent experimental and theoretical work on the CO oxidation reaction at "ruthenium" catalysts provides intriguing insight into the microscopic origins behind the frequently discussed pressure and materials gap between studies performed in ultra-high vacuum (UHV) and under realistic pressure conditions. Focusing on the Ru(0001) model catalyst, the considered system has, in fact, two important components to this issue. At first, an oxygen-rich environment changes the material from Ru to RuO_2. Thus, earlier ambient pressure studies on "ruthenium" catalysts were actually looking at an oxide film formed at the surface. Second, even after RuO_2 has been formed, the surface composition varies greatly with pressure: also, on the formed $RuO_2(110)$ there is a low-pressure surface phase that is routinely studied in UHV, but has little in common with the catalytically active situation.*

INTRODUCTION

Total or partial oxidation reactions, such as $CO + 1/2\,O_2 \rightarrow CO_2$ (CO oxidation) or $C_2H_4 + 1/2\,O_2 \rightarrow C_2H_4O$ (ethene epoxidation) form one of the most important classes of catalytic reactions, in total representing a multi-billion dollar industrial application [1]. The industrial catalysts presently employed for these processes typically contain late transition metals (TMs) such as Rh, Pd, Pt or Ag as the active material. These industrial catalysts are the product of a decade-long optimization process that often has highly sophisticated facets (*e.g.* combinatorial chemistry), but is in essence still nothing but a "trial and error"-type approach. Despite the obvious importance to our society, one thus has to admit that rationalized catalyst design is currently more a fiction than reality, which is largely due to the disturbing lack of atomic-scale understanding of the processes occurring at the catalyst surface under operating conditions.

This lack of understanding is not only caused by the complexity of industrial catalysts, but also by the scarcity of experimental techniques that would provide atomically-resolved information under the harsh environmental conditions of technological catalysis, which for oxidation reactions means oxygen partial pressures of the order of atmospheres and temperatures well above room temperature. With the real systems quite inaccessible, the classic idea of the "surface science" ansatz was to aim instead first at a rigorous understanding of much simpler model catalysts (often single-crystal surfaces) under the well-defined conditions of ultra-high vacuum (UHV), *i.e.* pressures that are more than 10 orders of magnitude lower than those in real technological catalysis. And after about forty years [2], it is probably fair to say that almost all of our present atomic-scale understanding of chemical processes at surfaces derives from studies of this kind. Sometimes this understanding can already (and with great benefit) be transferred to real catalytic applications, but often there are also blatant differences. This has been coined with the buzz words *materials gap* (single crystals *versus* supported nanoparticles, or change in the material structure) and *pressure gap* (UHV *versus* atmospheric pressures), and overcoming these gaps is probably one of the most important challenges in present-day surface science research.

The two gaps are furthermore often intertwined, and in recent years it has been recognized that one particular aspect of oxidation catalysis represents a prominent example for this: while traditional surface science research in UHV focused on studying the controlled adsorption and reaction of molecules on pristine TM surfaces, the latter might well oxidize under the technologically relevant ambient oxygen partial pressures. In turn, it could then be the formed oxide films at the surface that are really actuating the high-pressure catalysis, and not the transition metals that were investigated under UHV conditions. In this way, the difference in pressure goes hand in hand with a change in material,

preventing any direct correlation between the UHV surface science data and that recorded at technologically relevant pressure conditions.

A preeminent example for this is the CO oxidation at so-called "ruthenium" catalysts. The large discrepancy between the measured activities under UHV and ambient pressure conditions could only recently be resolved as resulting from the formation of a RuO_2 oxide film in the reactive environment. The corresponding large body of work performed on this surface provides unprecedented insight into the microscopic processes behind the general phenomenon called the pressure and materials gap. Here, this will be briefly summarized, revealing that the lessons learnt are most likely not just specific to this system.

1 OXIDE FORMATION IN THE REACTIVE ENVIRONMENT

Particular interest in the CO oxidation over Ru was originally triggered by work on supported catalysts by Cant *et al.* [3]. Under UHV conditions their "ruthenium" catalyst exhibited by far the lowest activity among the studied late transition metals, while under reactant pressures of the order of atmospheres the situation was reversed, and a superior activity compared with Pt, Rh or Pd was measured. Practically identical activities were subsequently obtained by Peden and Goodman [4], also for the Ru(0001) single crystal surface, on which I will focus from now on. This clear manifestation of a pressure gap could be resolved by extensive experimental and theoretical work, which showed that in oxygen-rich reactive environments RuO_2 forms at the surface [5-12]. While under UHV conditions the CO oxidation therefore takes place at the inactive Ru surface, the measured high catalytic activity in ambient conditions is instead actuated by the formed oxide film [8, 12-15].

At the Ru(0001) model catalyst surface, it is specifically a $RuO_2(110)$ film that is formed. Important steps in the oxidation of this surface are the formation of an on-surface O adlayer, followed by the penetration and accumulation of oxygen below the surface [9, 16, 17]. Continued oxidation could proceed via the formation of a metastable O-Ru-O trilayered film, which finally unfolds into the rutile RuO_2 bulk oxide structure, once a critical thickness is exceeded, as illustrated in Figure 1 [9, 18, 19]. Gas-phase conditions typical for technological CO oxidation catalysis ($p \sim 1$ atm, $T \sim 300-600$ K) fall deep inside the stability regime of this RuO_2 bulk oxide, indicating that thermodynamically nothing should prevent a continued growth of the oxide film once formed [20]. Interestingly, the hitherto observed $RuO_2(110)$ films never exceeded thicknesses of about 20 Å, even after long operation times [5, 7, 12]. This could be interpreted as reflecting kinetic limitations to a continued growth, *e.g.* due to slow diffusion of either Ru or O atoms through the formed film. More recent results further described below
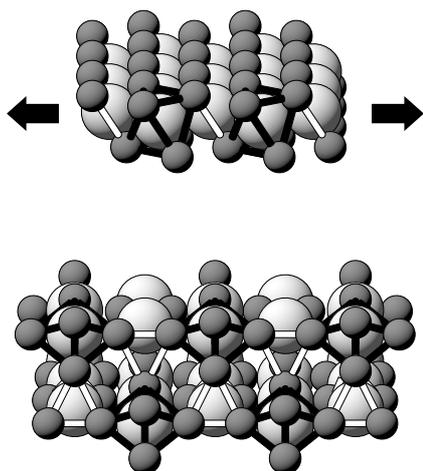
Figure 1

Perspective views of important atomic geometries in the oxide formation process at Ru(0001). Accumulation of sub-surface oxygen below the top Ru(0001) layer leads to the formation of an O-Ru-O trilayer (top panel). With increasing film thickness, the film switches to the bulk-like rutile RuO_2 structure (lower panel). This is achieved by simply stretching the trilayer in the direction of the arrows, keeping the length of the drawn O-O bonds (white and black lines) rigid. Note that these "bonds" do not refer to chemical bonds, but are merely used to guide the eye. Ru = large, light gray spheres; O = small, dark gray spheres (adapted from [9]).
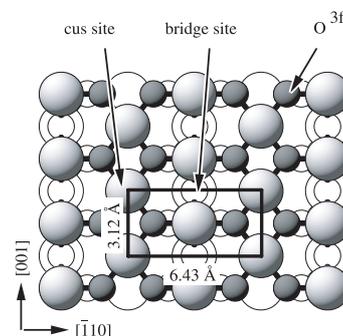

Figure 2

Top view of the $RuO_2(110)$ surface, showing the rectangular surface unit-cell, as well as the two prominent adsorption sites (bridge and cus) and the tightly bound 3-fold coordinated O^{3f} lattice oxygen. Ru = large, light gray spheres; O = small, dark gray spheres; atoms in deeper layers have been whitened for clarity.

suggest, however, that the reason is instead the kinetics of the ongoing catalytic reaction itself, which affects the surface composition in such a way that no further net diffusion through the film occurs. In other words, the oxidation reactions at the surface consume adsorbed oxygen atoms at such a pace that on average O penetration into the film occurs no more frequently than the filling of surface sites from inside the film [21].

2 CO OXIDATION AT RUO₂(110)

Instead of the pristine Ru(0001) surface, it is therefore a bulk-like crystalline $RuO_2(110)$ film at the surface that actuates the steady-state catalysis at ambient pressures. More specifically, it is the $RuO_2(110)$ facets themselves, and not macroscopic defects such as domain boundaries or steps. The latter are present, but have in this system only an insignificant influence on the catalytic function [10, 12]. Concentrating therefore on $RuO_2(110)$, Figure 2 shows a top view, explaining the location of the two prominent, under-coordinated adsorption sites offered by this surface. These are a bridge (br) site bridging two surface Ru atoms and a so-called coordinatively unsaturated (cus) site atop one surface Ru atom. The rutile bulk-stacking sequence would be continued by oxygen atoms occupying first all bridge

sites (leading to the so-called $O^{br}/-$ termination) and then all cus sites (O^{br}/O^{cus} termination). The $O^{br}/-$ termination is routinely observed experimentally after high temperature anneals in UHV, whereas the O^{br}/O^{cus} termination can be stabilized by oxygen post-exposure [10, 22-24]. Extensive theoretical work over the last years has shown that O and CO adsorption at other sites of the surface is energetically significantly less favorable than adsorption at bridge and cus sites [10, 23-26], which is consistent with all presently available experimental data [6, 10, 27-32].

This suggests that the catalytic activity of this surface can be understood in terms of the adsorption and desorption of O and CO at the bridge and cus sites, as well as diffusion and surface chemical reactions of reactants adsorbed at these sites. The metal oxide, once it is created, does not play an active role, *i.e.* under steady-state conditions there is no significant involvement of the tightly bound O^{3f} lattice oxygen atoms, *cf.* Figure 2. Instead, the catalysis is explained in terms of a Langmuir-Hinshelwood mechanism between adsorbed O and CO species at the surface. It should be stressed, however, that this comprises the involvement of unoccupied bridge sites, *i.e.* the frequently discussed O surface vacancies in the UHV $O^{br}/-$ termination.

First-principles calculations revealed only minor lateral interactions between the reactants when adsorbed at this

rather open oxide surface [26]. This allows one to quickly summarize the relevant features of the surface binding energetics as follows [26, 33]: oxygen atoms bind only with moderate strength to the cus sites (~ 0.9 eV/atom), whereas they bind quite strongly to the bridge sites (~ 2.3 eV/atom). CO adsorption, on the other hand, has a rather similar strength at both sites, namely ~ 1.3 eV/atom at the cus sites and ~ 1.6 eV/atom at the bridge sites. The barriers for the CO oxidation reactions can be nicely rationalized on the basis of these initial bound states. All in all there are four different reaction mechanisms possible between O and CO adsorbed at cus or bridge sites [26, 33]. The two reactions involving the strongly bound O^{br} species exhibit rather high barriers ($O^{br} + CO^{br}$: ~ 1.5 eV, $O^{br} + CO^{cus}$: ~ 1.2 eV), whereas the two reactions involving the moderately bound O^{cus} species exhibit lower barriers ($O^{cus} + CO^{br}$: ~ 0.8 eV, $O^{cus} + CO^{cus}$: ~ 0.9 eV). Just looking at these energetics, particularly the lowest-barrier $O^{cus} + CO^{br} \rightarrow CO_2$ reaction appears most relevant for the catalysis, and one would imagine it to dominate the overall activity.

3 STEADY-STATE SURFACE COMPOSITION AND ACTIVITY

Such a reasoning based only on the energetics neglects that the catalytic function is mostly the result of an intricate, if not concerted interplay between a large number of different molecular processes. Specifically, there are all possible kinds of adsorption processes of the reactants from the gas phase, diffusion on the surface, reaction events and desorption back into the gas phase. The interplay between these processes develops only over larger length scales, but is much more pronounced also over quite long time scales, since most processes at surfaces are rare, meaning that the time between consecutive processes can be orders of magnitude longer than the actual process time itself. Instead of the up to nanosecond time scales for individual elementary processes, the relevant mesoscopic system evolution resulting from the interplay of processes occurs then over time spans that can easily reach up to seconds, *i.e.* about 10 orders of magnitude longer.

A predictive modeling of the catalytic function based on microscopic understanding needs therefore to combine the accurate description of the individual elementary processes *with* an adequate treatment of how all these processes act together, in other words of their statistical interplay. Such methodology, generally termed "first-principles statistical mechanics" [34], is now becoming feasible, and has recently also been applied to the CO oxidation at $RuO_2(110)$ [25, 26]. The obtained steady-state average surface populations at $T = 600$ K are shown in Figure 3 as a function of the gas-phase partial pressures. Four different regions with defined surface structures can be discerned. At low CO partial pressures, these are the already discussed $O^{br}/-$ and O^{br}/O^{cus} terminations. Higher CO partial pressures stabilize additionally two further terminations. One with CO occupying all bridge sites and the cus sites empty ($CO^{br}/-$), and a fully CO-covered surface with CO at both sites (CO^{br}/CO^{cus}).

Since the detailed statistics of the elementary processes is explicitly accounted for in such mesoscopic simulations, it is straightforward to also evaluate the average occurrence of the reaction events over long time periods as a measure of the catalytic activity. The obtained turnover frequencies (TOF, in units of formed CO_2 per cm^2 per second) are shown in Figure 3, and are intriguingly peaked around a narrow range of gas-phase conditions. The computed TOFs in this "active state" are in quantitative agreement with the early experimental results by Peden and Goodman [4], and confirm that $RuO_2(110)$ is under these conditions indeed a very efficient CO_2 oxidation catalyst.
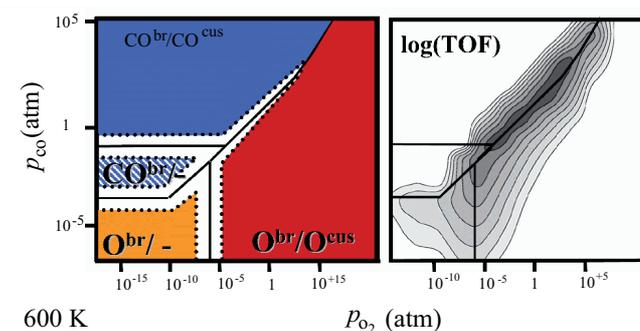

Figure 3

Left panel: steady-state surface structures of $RuO_2(110)$ in an O_2/CO environment, as obtained from first-principles kinetic Monte Carlo simulations at $T = 600$ K. In all non-white areas, the average site occupation is dominated ($> 90\%$) by one species, *e.g.* in the $O^{br}/-$ phase all bridge sites are occupied by oxygen atoms, while all cus sites are empty. See text for an explanation of the nomenclature of the other phases. Right panel: map of the corresponding catalytic CO oxidation activity, measured as turnover frequency (TOF, CO_2 conversion per cm^2 and second): white areas have a TOF $< 10^{11}$ $cm^{-2} \cdot s^{-1}$, and each increasing gray level represents one order of magnitude higher activity (from [25, 26]).

4 THE "ACTIVE STATE"

Contrary to the situation at most other partial pressures, the site occupation at bridge and cus sites in this active state is not dominated by one species, *i.e.* either O or CO (or vacant). Instead, the kinetics of the ongoing reactions builds up a surface population, in which O and CO compete for either site type at the surface. Figure 4 shows a snapshot of the surface in this active state, revealing that the distribution of the chemicals is neither purely random, nor ordered. It is important to realize that this spatial distribution is inherent

to the steady-state situation under these specific gas-phase conditions. While all four terminations with defined surface structures shown in Figure 3 could recently be stabilized and characterized in UHV [6, 10, 27, 29, 31, 32], the spatial distribution of the chemicals at the surface in the catalytically relevant active state is quite distinct from any of these terminations. The problem with *ex situ* UHV studies is obviously, that depending on the specific preparation recipe, quite different surface structures can be kinetically frozen in. These need then not have anything to do with the adsorbate composition built up by the intricate interplay of all surface processes under steady-state conditions. While cautious interpretation of corresponding experimental data does, in principle, provide a wealth of atomic-scale information, direct conclusions concerning the ambient pressure steady-state reactivity are therefore problematic.

The dynamics at the surface in the active state is furthermore extremely fast, and the average time adsorbed O atoms stay in bridge and cus sites before desorbing or being reacted away is only of the order of fractions of milliseconds. This goes hand in hand with huge fluctuations in the surface populations with time as shown in Figure 5. Remarkably, even at the bridge sites, where the O atoms bind very strongly, the average O occupation is only ~90%, and not 100% as in the surface terminations in pure oxygen environments. The rapid consumption of O atoms due to the ongoing catalytic reactions could therefore be the reason behind the afore-discussed limitations to continued oxide film growth.

The dynamic and disordered distribution of the surface chemicals in the active state leads to a number of surpris-ing properties [25, 26]. Most relevant in this context is that under these conditions of highest catalytic performance the chemical reaction with the most favorable energy barrier ($CO^{br} + O^{cus}$) contributes only little to the overall CO_2 production. In the active state, *cf.* Figures 4 and 5, there are simply too few CO^{br} available to initiate this reaction, and it is instead the $CO^{cus} + O^{cus}$ reaction that dominates the catalytic activity. Although the lowest barrier elementary process itself thus exhibits very suitable properties for catalysis, it occurs too rarely in the full concert of all possible processes to decisively affect the observable macroscopic functionality. This emphasizes the importance of the statistical interplay, and the novel level of understanding that can only be provided by first-principles-based mesoscopic studies that fully account for it.

5 CONCLUSIONS

The recent results on the CO oxidation at "ruthenium" catalysts briefly reviewed here provide intriguing insight into the microscopic origins behind the frequently discussed *pressure* and *materials* gap between studies performed in UHV and under realistic pressure conditions. Focusing on the Ru(0001) model catalyst, the considered system has, in fact, two important components to this issue. At first, an oxygen-rich environment changes the material from Ru to RuO_2. Thus, earlier ambient pressure studies on "ruthenium" catalysts were actually looking at an oxide film formed at the surface. Second, even after RuO_2 has been formed the surface composition varies strongly with pressure: also, on
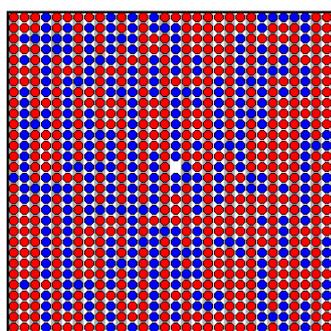

Figure 4

Snapshot of the steady-state surface population under optimum catalytic conditions at $T = 600$ K ("active state"). Shown is a schematic top view, where the substrate bridge sites are marked by gray stripes and the cus sites by white stripes. Oxygen adatoms are drawn as light gray (red) circles, and adsorbed CO molecules as dark gray (blue) circles (from [25, 26]).
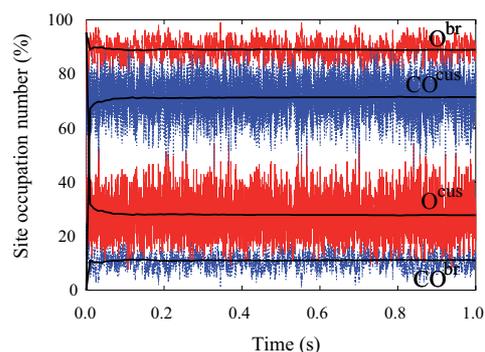

Figure 5

Time evolution of the site occupation by O and CO at the two prominent adsorption sites, bridge and cus, under optimum catalytic conditions at $T = 600$ K ("active state"). Under these conditions kinetics builds up a steady-state surface population in which O and CO compete for either site type at the surface, as reflected by the strong fluctuations in the site occupations. Note the extended time scale, also for the "induction period", until the steady-state populations are reached when starting from a purely oxygen-covered surface (from [25, 26]).

the formed $RuO_2(110)$ there is a low-pressure surface phase ($O^{br}/-$ termination) that is routinely studied in UHV, but has little in common with the catalytically active situation. In the latter, the kinetics of the ongoing reactions builds up a steady-state surface population with a complex disordered and dynamic distribution of the chemicals, which is quite distinct from any of the terminations that could hitherto be stabilized in *ex situ* UHV experiments.

While this shows how cautiously corresponding experimental data needs to be interpreted, the same lesson holds for theoretical studies. To some extent, a theoretical analogue of *ex situ* UHV studies would be to combine a first-principles computation of reactant binding energies in a few ordered configurations with reasoning based on the Sabatier principle and Brønsted-Evans-Polanyi relationships. With a computed very strong binding of oxygen to Ru(0001) this would have rationalized the low activity of this surface, but would have been incapable of explaining (let alone "predicting") the high activity of real "ruthenium" catalysts. Even considering the formation of an oxide film this approach does not yet provide the complete answer. Although the moderate bond strength of the O^{cus} species at $RuO_2(110)$ does now render the high catalytic activity comprehensible, a mere evaluation of the binding energetics and reaction barriers would have favored the wrong reaction mechanism. That the TOFs in the active state are not dominated by the lowest barrier reaction process results only from a proper consideration of the statistical interplay of all elementary processes. Such information is only provided by modern first-principles statistical mechanics methodology, which explicitly accounts for the correlations, fluctuations and spatial distributions of the chemicals at the catalyst surface. The reviewed example of CO oxidation at "ruthenium" catalysts illustrates the unprecedented insight that can be gained by such methodology, and we expect similar frameworks to soon be also applied to more complex reactions, possibly including selectivity issues.

ACKNOWLEDGEMENTS

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