

Oscillatory behavior in the CO-oxidation over bulk ruthenium dioxide – the effect of the CO/O₂ ratio

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Abstract

CO oxidation over polycrystalline ruthenium dioxide was monitored in an in-situ XRD setup. The evolution of the bulk state of the catalyst was followed by in-situ XRD during reaction, while the surface morphology and chemical state before and after reaction were investigated by HRSEM and EDX. The commercial RuO₂ powder was calcined prior reaction to ensure the formation of completely oxidized RuO₂. This pre-calcined RuO₂ is initially inactive in CO oxidation regardless of the CO/O₂ feed ratio and requires an induction period, the length of which strongly depends whether the catalyst is diluted with boron nitride or not. After this induction period oscillations in the CO₂ yield occur under O₂-rich conditions only. These oscillations exhibit two time constants for the diluted catalyst, while the low frequency oscillations were not observed in the case of undiluted RuO₂. Furthermore, the state of the catalyst after activation in O₂-rich feed conditions differs dramatically from the state after activation in CO-rich feed conditions. Firstly, the catalyst activated in an O₂-rich atmosphere remains inactive under CO-rich conditions in contrast to the catalyst activated in CO-rich conditions which is afterwards active under all feed ratios examined. Secondly, the surface morphology of the catalyst is quite different. While the apical surfaces of the RuO₂ crystals become roughened upon activation in the CO-rich feed, they become faceted under O₂ rich activation conditions. Therefore, we conclude that at least two different active surface states on the bulk RuO₂ catalyst exist.

Keywords: Ruthenium, CO oxidation, faceting, oscillations

1. Introduction

Within the platinum group metals ruthenium is expected to have the strongest impact on the pressure gap investigation in CO oxidation, as it shows the lowest activity under UHV conditions [1] while being a very potent catalyst at high pressures [2]. This issue was resolved by the finding that several oxygenated states of ruthenium, starting with the (1x1) chemisorbed oxygen layer and ending with RuO₂ are not accessible under UHV conditions [3]. There remain however, questions regarding the nature of working catalyst. Two opposite poles exist in the literature depending on the oxygen content in the oxygenated ruthenium system: on one side the (1x1) chemisorbed oxygen on Ru(0001) [2] and on the other side RuO₂(110) [4] and RuO₂(100) with the unsaturated fivefold ruthenium as the active cus-O sites. In a heavy debate [5-7] proponents of both sides in principle accept the presence of subsurface oxygen together with a so called transient surface oxide (TSO) [8;9] as a further possibility [3;7]. Recent in-situ

XPS measurements [10] showed that it is very hard to obtain only the (1x1) chemisorbed oxygen phase without forming subsurface oxygen and/or TSO during CO oxidation on Ru(0001). For that reason, to measure the activity of the intermediate (1x1) chemisorbed oxygen phase *alone* results in ambiguity. RuO₂ as the fully oxidized phase can be reached during CO oxidation reaction [10;11], however care must be taken in order to exclude the intermediate subsurface oxygen/TSO. Recent investigations by Flege et al. [12] shows nicely the coexistence of all three states during oxidation of Ru(0001) with NO₂. In this context it would be very helpful to study the single crystalline RuO₂ but unfortunately only one surface science study of single crystalline RuO₂ is known [13]. Therefore, we decided to study the largely defined stoichiometric catalyst, polycrystalline RuO₂, in CO oxidation. In-situ XRD was employed to investigate the bulk phase(s) of the catalyst under reaction conditions. However, as we have already shown in a previous publication [14], the bulk state of the catalyst does not correlate directly with the observed activity. From

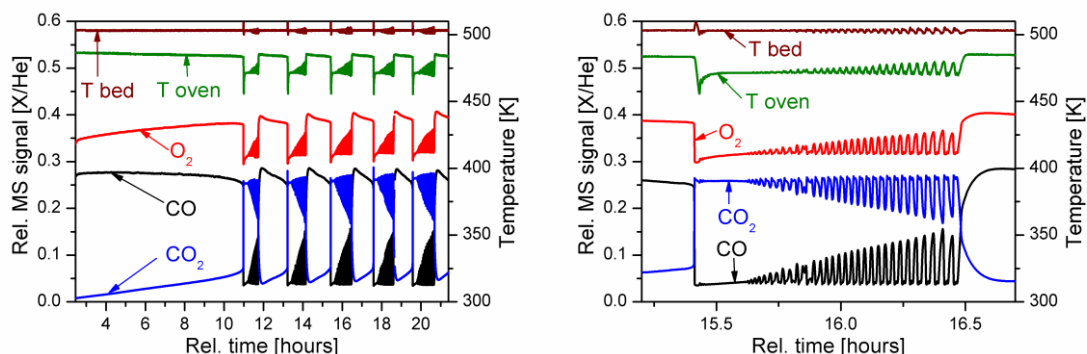


Fig. 1: (Color online) On the left the activation of the RuO₂ in oxygen-rich feed (*diluted* with BN; CO:O₂ 5:10) at 503 K is shown. After a long induction period ignition occurs and a complicated oscillation pattern with two time constants is observed. (The increase of the oxygen MS signal during the induction period, although scaled by Helium, is due to the change of the MS sensitivity in oxidizing feed conditions.) On the right the high frequency oscillations are shown in detail.

XRD, pure bulk RuO₂ was observed in both active and inactive states, while active catalysts may show bulk RuO₂, Ru metal, or mixtures thereof. In detail we reported that surface reduced polycrystalline RuO₂ was immediately active in CO oxidation while fully oxidized RuO₂ (confirmed by XRD and/or EDX) was not. In this recent study, questions about the surface and bulk state after activation in oxygen rich feed as well as the nature of the observed oscillations with two very different time constants emerged. In principle, the low frequency oscillations could stem from changes in the bulk. The surface morphology and overall stoichiometry of the RuO₂ particles was studied by HRSEM and EDX.

In the present paper we show that at least two active surface modifications exist on bulk RuO₂. One or both of these is highly active under net-oxidizing conditions but hardly active under net-reducing conditions. This result could help to explain the different activity of polycrystalline RuO₂ observed by Narkhede et al. [15] under different CO/O₂ feed ratios.

2. Experimental

The catalytic experiments were carried out in an in-situ XRD setup described in detail in a previous paper [14]. Briefly, a STOE Theta/theta X-ray diffractometer (CuK α radiation, secondary graphite monochromator, scintillation counter) is equipped with an Anton Paar XRK 900 in-situ reactor chamber. The temperature was measured by two type-K thermocouples. While the first one was in close contact to the catalyst bed (labeled Tbed), the second thermocouple was situated near to the gas inlet (labeled To-ven). The temperature reading of the second thermocouple was generally below the temperature of the catalyst bed due to the cooling effect of the incoming gases. Gases with purity > 99.999 % for He and O₂ and > 99.997 % for CO were supplied by mass flow controllers (Bronkhorst). CO oxidation was carried out mainly under net oxidizing

(CO/O₂: 5/10; 10 Nml/min O₂) but also under net reducing (CO/O₂: 14/1; 1 Nml/min O₂) and stoichiometric (CO/O₂: 10/5; 5 Nml/min O₂) feed conditions. The total flow rate was always set to 100 Nml/min by adding He to the mixture.

As already mentioned in an earlier paper [14] commercial RuO₂ powders are typically not homogeneous single phase RuO₂ as evidenced by XRD. Furthermore, EDX generally reveals some aggregates of particles with an overall stoichiometry of RuO. In a series of experiments, it transpired that calcination in pure oxygen at temperatures well above 1000 K was necessary to obtain pure RuO₂ (according to XRD and EDX) from the as-purchased material. Consequently, the commercial RuO₂ powder used (Acros organics), in which XRD had revealed traces of Ru metal, was calcined at 1073 K in 30 Nml/min pure oxygen for one hour. The resulting catalyst was used either pure or mixed with hexagonal boron nitride (325 mesh) in a weight ratio of 3:5. Blank experiments were carried out with pure BN. No significant CO₂ formation was observed. The effluent product gas composition and thermocouple readouts were monitored with a Pfeiffer OmniStar quadrupole mass spectrometer. The reactor was assumed to operate as a packed bed flow-type.

The HRSEM experiments were conducted in the secondary electron mode with a Hitachi S-4800 (FEG) instrument equipped with an EDAX Genesis4000 system for energy dispersive X-ray (EDX) analysis. Low acceleration voltages of 2 kV were used for the micrographs in order to enhance the surface sensitivity. EDX spectra were obtained by using an accelerating voltage of 5 kV. After cooling down in the reaction atmosphere the samples were directly transferred (exposed to air) from the reactor to the SEM without further treatment.

The electron backscatter diffraction (EBSD) measurements were performed with a Nordlys-II-detector from HKL technologies and a Hitachi S-2700 SEM at the Zentraleinrichtung Elektronenmikroskopie (ZELMI) at the TU Berlin.

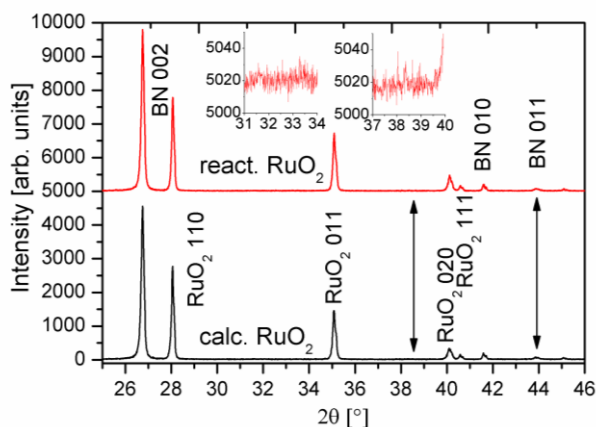


Fig. 2: (Color online) Representative XRD patterns of *diluted* calcined RuO₂ and of the reacted state after activation/oscillations under net-oxidizing conditions (offset for clarity). The arrows mark the positions where the Ru 010 and Ru 011 peaks of the ruthenium metal are expected. The region for the Ru 010 peak ($2\theta = 37\text{--}40^\circ$) as well as a region without peaks ($2\theta = 31\text{--}34^\circ$) is magnified in the inset for the (*diluted*) reacted RuO₂ revealing no metallic ruthenium contribution.

3. Results

3.1. In-situ XRD and catalytic tests

In order to verify the results obtained in a conventional packed bed reactor; i.e. firstly the oscillation behavior of the activated RuO₂ in an oxygen-rich feed and secondly the necessary additional induction period after exposing the oxygen-rich feed activated catalyst to a CO-rich feed [14], we have tried to reproduce these results in the quite different in-situ XRD reactor. Additionally we studied the *undiluted* catalyst under net-oxidizing and net-reducing conditions at the end of this part. As shown in figure 1, the characteristic behavior of the diluted catalyst under oxygen-rich feed conditions could be reproduced: After the catalyst bed reaches the set point temperature 503 K a small quantity of CO₂ is produced, of the same order as the blank conversion. During several hours at 503 K the activity increases slowly until an abrupt ignition occurs. High frequency oscillations (with frequencies around 0.01 Hz) then start at this stage of high conversion with increasing amplitude. After approximately half an hour extinction leads to a conversion level similar to that observed before initial ignition, resulting in a low frequency pattern. Both of these frequency patterns of CO conversion are stable over several hours. Throughout this paper, unless otherwise stated, XRD shows no differences between RuO₂ after reaction and RuO₂ after calcination. One may anticipate that the activation of RuO₂ could be accompanied by a slight change in the bulk stoichiometry (i.e. RuO_{2-x}), which in turn should influence the lattice parameters.

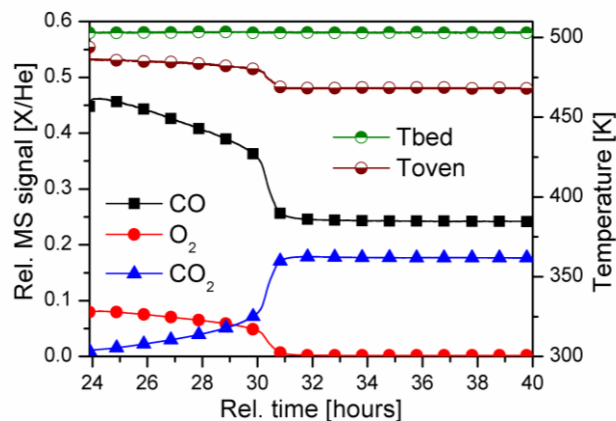


Fig. 3: (Color online) After activation of the with BN *diluted* RuO₂ in oxygen rich feed (see fig. 1) the catalyst again requires a very long induction period before ignition in CO rich feed conditions (CO:O₂ 12:3) at 503 K.

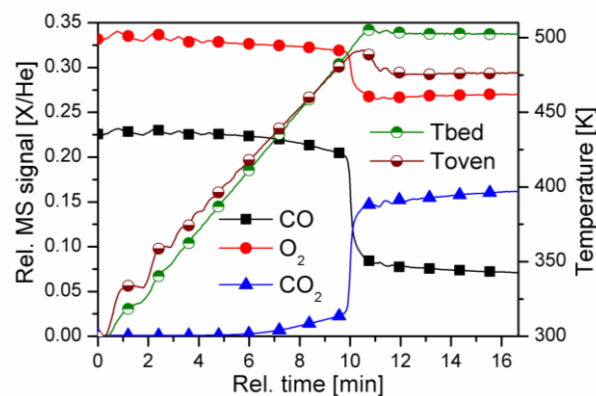


Fig. 4: (Color online) Ignition of the reaction in the case of *undiluted* RuO₂ in the O₂-rich feed (CO:O₂ 5:10) occurs during the temperature ramping at ~ 480 K. After ignition the activity increases slowly with complete conversion of CO within hours (not shown).

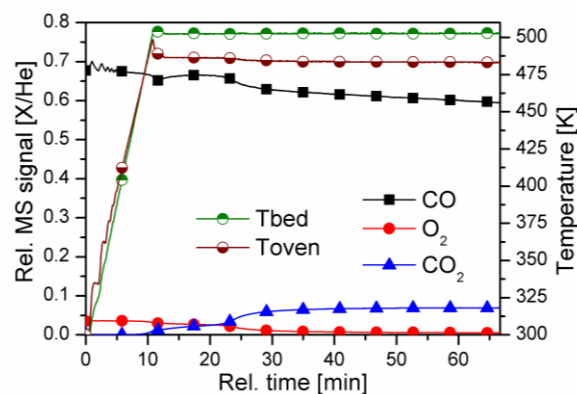


Fig. 5: (Color online) The activation of *undiluted* RuO₂ in CO rich feed (CO:O₂ 14:1) at 503 K is accomplished after several tenths of minutes. In contrast to this result the induction period for the *diluted* RuO₂ lasts several hours [14].

Unfortunately, such subtle changes are beyond the limits of detection in the current context, as the lattice parameters are influenced more strongly by temperature changes than by stoichiometry differences.

As already discussed in reference [14], the strongly exothermic nature of CO oxidation may readily lead to local overheating, with documented temperature differences of up to 50 K for the area sampled by the X-ray beam in our setup. Consequently, the local temperature of the catalyst corresponding to the XRD signal, and thus the observed lattice parameters, are necessarily a function of catalytic activity. This somewhat limits the utility of XRD under reaction conditions primarily to bulk phase identification.

Careful comparison of XRD data obtained at 25 °C in the in-situ cell before and after activation/oscillations under net-oxidizing feed however, reveal no changes in the bulk RuO₂ phase within the limits of detection (figure 2). The tetragonal lattice parameters of RuO₂ were calculated to $a = 4.49455(8) \text{ \AA}$, $c = 3.10804(6) \text{ \AA}$ after calcination and $a = 4.49472(7) \text{ \AA}$, $c = 3.10824(6) \text{ \AA}$ for the reacted RuO₂ (the estimated standard deviation are given in parentheses).

The thus activated catalyst was quenched during the high activity phase (high frequency oscillations) by switching off the oven and the reaction atmosphere was changed at room temperature to the CO-rich feed (CO:O₂ 12:3). After the temperature ramp to 503 K limited CO₂ production is again observed, however it takes several hours until ignition occurs (fig. 3). During the complete conversion the catalyst is reduced slowly as revealed by in-situ XRD.

A completely different picture emerges if **undiluted** RuO₂ is used for CO oxidation. The reaction ignites within several minutes in both cases, i.e. oxygen-rich and oxygen-poor feed conditions (fig. 4 and 5). While ignition in the case of oxygen-rich feed conditions occurs immediately during the initial temperature ramp at around 480 K, in the case of the CO-rich feed, the reaction starts more slowly, with two s-shaped functions observed (fig. 5). Interestingly, the low frequency oscillations under oxygen-rich feed conditions are no longer observable, while the high frequency oscillations still occur with frequencies around 0.03 Hz (not shown). As the amount of RuO₂ is approximately equal in all cases (~ 30-40 mg) the main difference is the increased heat conductivity of the undiluted catalyst. To clarify this issue a small gold foil (~ 0.1x2x2 mm³) was buried in the middle of the catalyst bed (14 mm in diameter, diluted RuO₂). In this case the reaction ignites already after approximately three hours (not shown) which corresponds to one third of the induction time required without gold.

To elucidate the nature of the surface after activation in oxygen rich feed we investigated the catalyst with high resolution SEM.

3.2. SEM

As already discussed in an earlier paper [14], the pronounced octagonal habit of the large calcined RuO₂ crystallites is not the expected one for a tetragonal crystal system with two different surface free energies for the {100} and {110} surfaces [3]. As such, we have conducted EBSD measurements. These measurements allow indexing of the surface orientations of small crystallites. The first result is that all of the investigated large crystallites are single crystalline i.e. one particle gives only one EBSD pattern at every position of the electron beam. The second result is the indexing of the surfaces. As long as the typical habit was observable, the small triangular apical surface was always indexed as a {111} surface. Figure 6 shows a typical example of the calcined RuO₂.

While activation of the calcined RuO₂ in CO-rich feed conditions leads to roughened apical surfaces with reduced stoichiometry [14], activation under oxygen-rich feed conditions leads to strong faceting of the apical surfaces. Figure 7 shows a typical crystallite after activation of the diluted catalyst.

The magnified micrograph (figure 7) reveals the unchanged nature of the lateral surfaces as well as the strong faceting of the {111} and {101} surfaces. All investigated crystallites exhibit more or less pronounced this faceting of the apical surfaces. For this reconstruction in the nm range significant material transport is necessary. The faceting of the {111} surface consists of small facets compared to the {101} which shows more large facets. EDX shows the stoichiometry of the apical and lateral surfaces to be RuO₂.

The reconstruction of the apical surfaces is similar for the activated undiluted catalyst under oxygen-rich conditions. In figure 8 the magnified micrograph reveals the very complex nature of the {111} surface reconstruction. Very heavily reconstructed apical surfaces are observable, in particular for the undiluted catalyst which undergoes fast activation. Figure 9 shows one of those where the indexing is hampered due to the heavy reconstruction. The shown apical surface is however assigned as {101} due to its large size.

4. Discussion

Onken and Wicke [16] demonstrated that in CO oxidation over supported Pt even small temperature variations at the gas entrance (0.5 K) to the catalyst bed could lead to strong ignition extinction behavior. In their case heat transfer is effected predominately through the gas-phase. In our case it appears that direct heat transport between solid particles also plays a crucial role. We therefore assign the drastic differences in the induction times between the diluted and undiluted RuO₂ to the different heat conductivities. The absence of the low frequency oscillations under net-oxidizing conditions with undiluted RuO₂ revealed this type of oscillations as heat transfer induced. It is however,

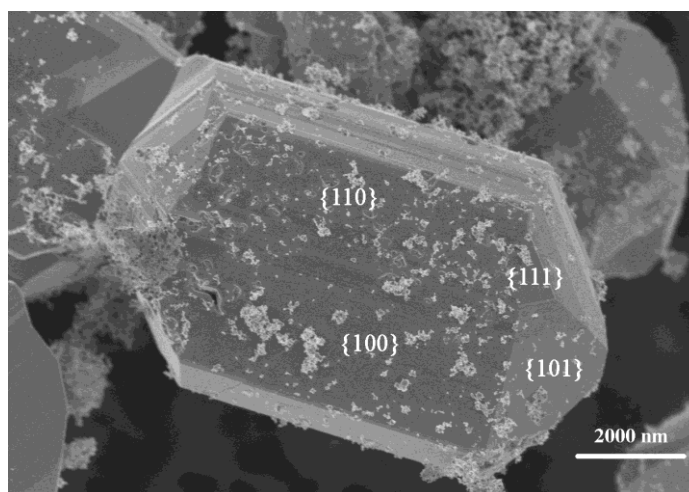


Fig. 6: The SEM micrograph shows the typical habit of a RuO₂ crystal after calcination. Indexing with EBSD reveals the lateral {110}, {100}, and apical {101}, {111} facets as shown (the curly brackets are used for the family of symmetry-equivalent facets). In addition to the large crystals, very small particles are also observed in all cases.

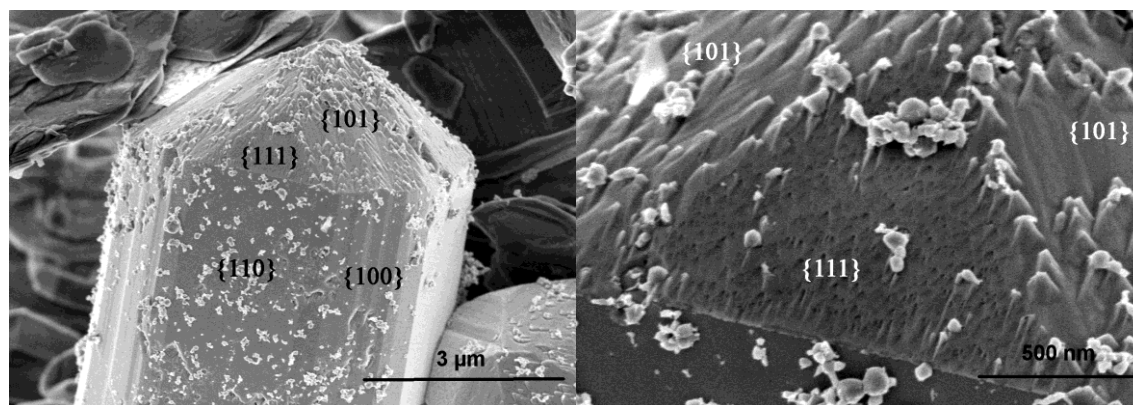


Fig. 7: SEM micrographs of the *diluted* catalyst after activation in oxygen-rich feed. The initial habit is still observable and allows indexing of the surfaces. The apical surfaces are strongly faceted. In the magnified micrograph of the same crystallite on the right the different reconstructions of the {111} and {101} surfaces become obvious.

prudent to mention here one result of a previous paper [14], namely that with BN *diluted* RuO₂ with partly reduced surfaces as well as the heavily reduced oxygenated ruthenium, ignites during the initial temperature ramping in the 380 – 420 K temperature range under all feed conditions. One conclusion of this is that those reduced surfaces either on bulk Ru or bulk RuO₂ are active. That is why we conclude that a necessary induction period points to an initially inactive catalyst.

The activation of initially inactive (fully oxidized) RuO₂ in an oxygen-rich feed leads to the formation of RuO₂ crystallites with faceted apical surfaces. These apical facets are active under net oxidizing conditions *only*. Under net-reducing conditions a very long induction period is again necessary to ignite the reaction and thereafter the catalyst reduces slowly to yield the roughened surfaces known to result from observations detailed in a previous paper [14]. Based on our SEM observations the induction

period under net-oxidizing conditions could be explained in a similar way as on Pt(110) ([17] p. 707-708 and references therein) by the faceting of the apical surfaces while under net-reducing conditions the reduction of the near surface region seemed to be essential.

In the literature there is agreement that the activity of the catalyst is strongly dependent upon the CO/O₂ ratio of the feed. Until now the different activity of oxygenated ruthenium at different feed ratios has been explained in the literature by deactivation processes (see another study of polycrystalline RuO₂ by Narkhede et al. [15]). Under net-oxidizing conditions the development of the completely inactive c(2x2)-RuO₂(100) reconstruction should be responsible, while under net-reducing conditions oxygen depletion results in the formation of inactive ruthenium metal. Thus, to the best of our knowledge, this is the first time that a special oxygenated ruthenium state is reported to be active under net-oxidizing conditions *only*. This find

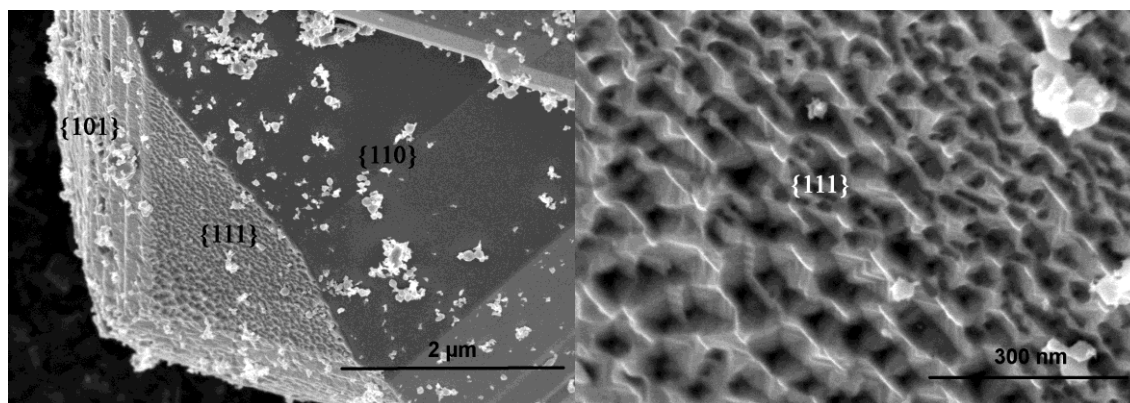


Fig. 8: SEM micrographs of the *undiluted* catalyst after activation in oxygen rich feed. Again the apical surfaces are reconstructed but more pronounced. In the magnified micrograph of the same crystallite on the right the complex faceting of the (111) surface is shown.

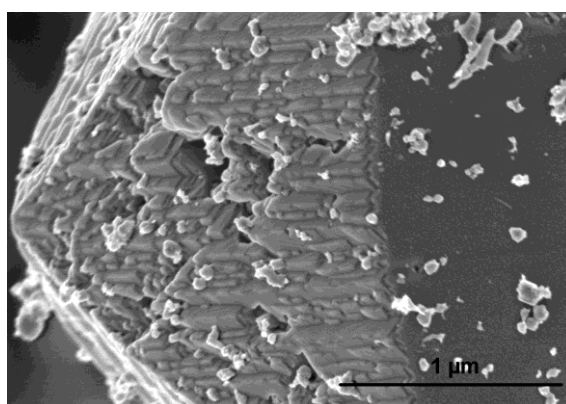


Fig. 9: SEM micrograph of a heavily reconstructed catalyst. The assignment of the facet index is already hampered due to the heavy reconstruction but is most likely the apical (101) facet. The catalyst was undiluted and activated in an oxygen-rich feed.

ing could also explain the increasing activity for net-oxidizing, net-reducing and stoichiometric feeds found by Narkhede et al. [15] for polycrystalline RuO₂: While the apical surfaces in the faceted form are active under net-oxidizing conditions solely, the sum of the activity of *all* crystallite surfaces yields the aforementioned increase in activity. The unambiguous assignment of surface facets is unfortunately not possible from our data. Of course, one could try to assign the triangular shaped facets of the heavily faceted crystallite in fig. 8 as {110} facets and explain the high frequency oscillations with the formation and removal of the inactive c(2x2)-RuO₂(100) reconstruction. This however, would lead to the question as to why these {110} facets are inactive under the net-reducing conditions. Thus, the formation of {110} and {100} surface facets is unlikely. However, the strong material transport thereby makes the alternatively appearance of surface facets likely. Here we can only speculate whether two types of facets with differing activity similar to the case of CO oxidation on Pt(110) [17] or one type of inactive facets and an active intermediate state (during the material transport) is responsible for the oscillations. Another thinkable explanation could include also for the high frequency oscillations heat transport phenomena under our specific conditions.

Interestingly, this strong faceting of the apical surfaces was not observed with the calcined RuO₂ crystallites. A possible scenario in net-oxidizing feed conditions should therefore make use of the reducing property of CO which is absent during calcination: While the fully oxidized apical surfaces are stable the partly reduced surfaces (by CO) are not and lead to surface reconstruction by surface migration or gas phase transport via volatile RuO_x species. The latter process requires high local concentrations of oxygen to form the volatile higher ruthenium oxides. This alone does not answer why these proposed surface oxygen depleted faceted surfaces are not active under CO-rich conditions. Here theory could help: In a recent paper Reuter and Scheffler have shown by first-principles kinetic Monte Carlo simulations that the *in principle* active RuO₂(110) surface could be either completely covered by CO or O₂ depending on the feed ratio, resulting in very low activity, but with the highest TOFs reached when the adsorption state of CO and O₂ is disordered and very dynamic [18]. The oxygen-rich feed may mimic this high conversion state while the CO-rich feed may lead to fully CO covered surfaces and again, in an activated process, to further reduction of the sample. Within this theoretical model the observed oscillations could *in principle* be explained by the

change of the CO and O₂ ratio in the adsorption state due to depletion of the CO in the gas phase at high activity. Under reducing conditions these oscillations never occur because of the further oxide reduction to TSO and subsurface oxygen. The faceting is, however, completely missed within this model.

Finally it could also be a conceivable possibility that a partly reduction of the near surface region not measurable with the not surface sensitive methods EDX and XRD is responsible for the observations. This reduction leads to the transient surface oxide and subsurface oxygen [10]. These oxygenated ruthenium states were never reported to be inactive under reducing feed conditions. Moreover, it was observed that all reduced surfaces either on bulk RuO₂ or Ru are active independent of the feed ratio [14]. The result of the again necessary induction period under net-reducing conditions of the already active catalyst under net-oxidizing conditions makes this possibility of surface reduction implausibly.

5. Conclusion

The high and low frequency oscillations under oxygen-rich feed conditions in a conventional packed bed reactor [14] could be reproduced in an in-situ XRD setup. Under net-oxidizing feed conditions the initially inactive pre-calcined RuO₂ becomes active in CO oxidation and remains as RuO₂ in the bulk. The active catalyst exhibits pronounced faceting of the apical {111} and {101} surfaces. Under net-reducing conditions this material is again initially inactive. A long induction period, leading to par-

tially reduced RuO₂ or oxygenated ruthenium metal, is required in order to observe activity. The distinctly shorter induction period of undiluted RuO₂ and the missing low frequency oscillations reveal the strong influence of inter-particle heat transfer.

The faceted surfaces active only under oxygen-rich feed conditions may be one reason for the observed strong dependence of the activity on the CO/O₂ feed ratio. Only a very small part of the RuO₂ surface is highly active under net-oxidizing conditions.

These faceted surfaces unlikely exhibit RuO₂ {100} or {110} facets because of the observed initial inactivity in CO-rich feed conditions, the same holds for partly reduced RuO₂ in the surface region, i.e. subsurface oxygen and transient surface oxide. This result indicates the need to invoke increased complexity of the working oxygenated ruthenium catalyst to incorporate faceted {101} and {111} surfaces as a second active surface modification of bulk RuO₂ beneath the reduced surface.

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