Oxidation of methanol on Ru catalyst: Effect of the reagents partial pressures on the catalyst oxidation state and selectivity

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Abstract
In situ core level photoelectron spectroscopy and mass spectrometry have been utilized to study the methanol oxidation on a model RuO2 catalyst at pressures ranging from 10^{-6} to 10^{-1} mbar. The experiments were carried out varying the O2/CH3OH molecular mixing ratio from 0.25 to 3.3 and the reaction temperature from 350 to 720 K. The Ru 3d 5/2 and O 1s core level spectra were used to characterise the dynamic changes in the Ru oxidation state by exposing the oxide pre-catalyst to different reagents partial pressures and temperatures. Full oxidation to CO 2 + H2O or partial oxidation to CO + H 2O + H2 have been observed in the whole pressure range for specific reaction conditions, which preserve the oxide catalyst state or reduce the oxide to metallic Ru. The selective oxidation to formaldehyde is observed only at pressures in the 10^{-1} mbar range, catalyzed by a RuOx surface oxide formed by partial reduction of the oxide pre-catalyst.

Keywords: Ruthenium; Methanol; Oxidation; Formaldehyde; High-pressure XPS; Mass-spectrometry

1. Introduction

The catalytically active state under reaction conditions is still a very disputable issue. In the particular cases of oxidation reactions the classical oxygen source considered in modelling the reactions mechanism is the lattice oxygen on nearly stoichiometric surfaces of metal oxides (Mars–van Krevelen mechanism) [1], or adsorbed oxygen on metal surfaces. In both cases, the consumed surface oxygen is restored by the O2 reactant in the gas phase.

In reality, the catalytically active state is not necessarily the well-defined oxide phase, and possible differences in the so-called ‘oxidation state’ of the surface and the bulk have already been considered [2]. Studies of selective oxidation of CH3OH on Cu have provided clear evidence for catalytically active state with incorporated subsurface oxygen, which can be described as a disordered surface oxide film [3,4]. Such surface oxide states are in fact the transient precursors towards formation of metal bulk oxides, which nucleate and grow when a critical amount of oxygen is incorporated subsurface [5]. The calculated temperature–pressure (T, P O2 ) phase diagrams attempting to predict the thermodynamically stable phases under realistic oxidation conditions confirm that the oxidation of transition metals is a rather complex process with phase coexistence regions [6–8]. In realistic oxidation reactions the second reactant usually acts as a reducer (e.g. CO, H2, CH3OH or other organic molecules) and affects the (T, P O2 ) space of oxidation phases driving the oxidation state away from the equilibrium achieved in a pure O2 ambient. Consequently, when the reactions have several possible pathways the selectivity and the corresponding catalytically active state can be controlled by varying the reaction temperature and chemical potentials (partial pressures) of the reactants.

In the last decade a main challenge of the surface science UHV experiments is that often enough the extensive knowledge about important elementary processes at the model catalyst’s surface cannot be directly extrapolated to the catalytic processes occurring at ambient pressures, when the chemical potentials of reagents in the gas phase become important. In this respect Ru, a catalyst used in exhaust gas converters and fuel cells is a textbook example of the so-called ‘pressure gap’ in oxidation and catalyst activity. Under UHV conditions the Ru catalyst turned out
to be completely inactive for CO oxidation due to the kinetic limitation for accumulation of oxygen to form the catalytically active surface at the low oxygen potentials in the traditional surface science experiments [9–11]. The crucial role of the PO2 became apparent in a number of recent investigations showing that it is a prerequisite for formation of the catalytically active phases, namely a thin surface oxide film (RuOx) at T < 550 K and a stoichiometric well-ordered RuO2\(2\) \(1 1 0\) phase at T > 550 K [10,12–14]. Extensive structural, photoemission and TPD studies characterized the lower temperature Ru oxidation state as a disordered RuOx with 1–4 ML oxygen incorporated within the top few Ru layers, which also precedes the nucleation and growth of the stoichiometric RuO2 phase at higher temperatures [14]. They have also provided evidence for the coexistence of RuOx with the RuO2 phase in a wide (T, PO2) range.

One of the approaches to narrowing the pressure gap, used in our previous study of CO oxidation on a Ru(0001) catalyst, is monitoring the catalytically active state and products in the gas phase by in situ mbar–bar pressure X-ray photoemission spectroscopy (XPS) and mass-spectrometry [3]. We found that below 500 K, when the formation of RuO2 is kinetically hindered, the surface is already activated for CO oxidation by formation of the precursor surface oxide, RuOx [15]. The actual surface state of the catalyst dynamically changed with temperature and CO/O2 partial pressures. Both the RuOx ‘surface oxide’ and RuO2 phases can easily be reduced into an inactive Ru metal with adsorbed oxygen in excess of CO and Ru can be re-oxidised in an excess of oxygen regaining the catalytic activity. The active role of subsurface oxygen and formation of surface oxide RuOx have also been considered in catalytic behaviour of Ru electrodes in fuel cells [16,17].

The CO oxidation is a simple single-channel reaction system, which cannot tackle the ‘pressure gap’ in catalyst selectivity, another very important issue addressed by the present study of CH3OH oxidation on a model Ru(0001) catalyst. CH3OH catalytic oxidation is a complex process with long list of possible reactions involving different intermediates and final products, which also depend on the catalyst chemical state [18,19]. The first common step on both metal and oxide surfaces is H abstraction, yielding H\(_2\) or OH and methoxy, CH\(_3\)OH, where the subscript ‘s’ indicates that the species is bonded at the surface. In the presence of oxygen further activation of the C-H bonds in CH\(_3\)OH, through red-ox cycles leading to H\(_2\), CH\(_2\)O, CO, CO\(_2\), and H\(_2\)O (products of partial or complete oxidation), passes through the following principle intermediates: OHs, Hs, CH\(_2\)Os, CO, and HCOOs. The CO\(_2\) can result of decomposition of the HCOO, or secondary oxidation reaction of CO. Starting with an oxidised Ru(0001) catalyst, considered to be the catalytic active state for CH3OH oxidative-dehydrogenation to CH\(_2\)O + H\(_2\)O [20], we followed in real time the products yield and the evolution of Ru oxidation state and adlayer in the 10\(^-6\) to 10\(^-7\) mbar range varying the (T, PO\(_2\), PCH\(_3\)OH) space.

### 2 Experimental

The experiments were performed at the synchrotron radiation facility BESSY in Berlin in the high pressure XPS station designed and constructed in the FHI-MPG [21]. The sample, mounted inside a reaction cell, 2 mm away from the entrance aperture to the differentially pumped hemispherical analyser Phoibos 150 (SPECS GmbH), was heated from the backside using an infrared laser system. The CH3OH and O2 gas flows and the products released in the gas phase were monitored by a Hiden mass spectrometer. The fragmentation patterns of the reactants and products and the sensitivity factors were considered in the determination the molecular mixing ratio of the reagents and the relative yield of the products. In particular, this concerns the CH2O and CO yields, which should be corrected for the attenuation of the CH3OH-related mass signals 30 and 28 due to CH3OH consumption. The relative decrease of the mass 31 was used as a measure of the methanol conversion. The Ru(0001) sample was cleaned before each reaction cycle using the well established procedures [12,22] and then oxidised to form a RuO2 phase with thickness of 5–10 nm. All photoelectron spectra were normalized to the photon flux, monitored by a photodiode. The Ru 3d and O 1s spectra were measured in normal emission with photon energies of 450 and 650 eV, respectively and overall spectral resolution of 0.3 eV. According to the universal curve for the electron mean free path [23] the effective escape depth for the O 1s and Ru 3d photoelectrons is ~5 Å, which limits the probing depth to the top few layers (~10 Å).

The dynamic response of the O 1s and Ru 3d\(_{3/2}\) core level spectra was used for precise assignment of the catalyst oxidation state, which was correlated to the corresponding yields of the products of methanol oxidation. CO, CO\(_2\), H\(_2\), H\(_2\)O and CH\(_2\)O, detected with the mass spectrometer in our experiments. The already available Ru 3d\(_{5/2}\) and O 1s core level spectroscopy data provided the necessary basis for identification of the Ru oxidation states (metallic Ru with adsorbed oxygen, RuOx ‘surface oxide’, and RuO2) and the ad-species (see Table 1). For the Ru(0001) surface the intensity ratio between the overlapping O-related Ru 3d\(_{3/2}\) component at 280.5–280.6 eV, accounting for both adsorbed oxygen and RuOx and the bulk component, Ru\(_{bulk}\), turned out to be the best fingerprint for differentiation between adsorption oxygen state with coverage 0.33–0.67 ML on Ru(0001) and RuOx. For the RuOx state, detected under our experimental conditions this ratio was significantly higher for than the characteristic ratio of 0.3 for 0.67 ML of adsorbed oxygen and reaches ~0.6 for ~4 ML incorporated oxygen. The Ru 3d\(_{3/2}\) and O 1s spectra of the initial oxide pre-catalyst, prepared by in situ oxidation of Ru(0001) at 720 K and 10\(^1\) < P\(_{O2}\) < 1 mbar contained only the characteristic features of the RuO2 at 280.75 and 529.5 eV, respectively.
3. Results

The evolution of the catalyst chemical state and ad-layer composition and the corresponding catalyst activity were studied for different temperatures and partial pressures of O2 and CH3OH in the 10^-6 to 10^-1 mbar range. Most of the experiments were carried out at oxygen potentials supposed to favour partial oxidation reactions, particularly focused on the selective oxidative dehydrogenation to formaldehyde, the product of industrial importance. As reported below sensible formaldehyde production was monitored only in the 10^-1 mbar range and conditions for high selectivity were obtained at T > 450 K for O2/CH3OH molecular mixing ratio (MMR) of 0.6. Since it is naive to narrow the pressure gap by maintaining a constant O2/CH3OH partial pressure ratio experiments varying the MMR were performed as well.
The presence of RuO$_2$ and RuO$_x$ components in the Ru 3d$_{5/2}$ spectra before exposure to the reactants mixture correspond to the RuO$_2$ state (peaked at 529.5 and 280.8 eV). The O 1s spectrum undergoes significant changes after introducing the CH$_3$OH reactant. The broad multi-component feature growing on the high-energy side of the O 1s spectra results from the OHs and CH$_x$Os ad-species, derived from CH$_3$OH dissociative adsorption. The O 1s components giving the best fit of the O 1s spectra in Fig. 1(a) are in fair agreement with the binding energies of OH$_x$, CH$_3$O$_x$ and CH$_2$Os species on a RuO$_2$(110) surface (see Table 1). The attenuation and extinction of these O 1s components in the 390–500 K range mark desorption of the CH$_3$OH-related ad-species. The small shift of the component assigned to OH$_x$ at 390 and 460 K may be due to overlap with the emerging CO$_x$ component resulting from further dehydrogenation of CH$_3$O$_x$ species. At MMR = 0.6 the oxide catalyst state is preserved up to temperatures of ~ 470 K. At 480 K the measured Ru 3d$_{5/2}$ spectrum is still dominated by the RuO$_2$ component but it starts to broaden on the low energy side due to the emergence of a component at ~280.5 eV of the partially reduced RuOx phase. Above this temperature the Ru bulk component also emerges in the Ru 3d$_{5/2}$ spectra indicating sensible partial reduction of RuO$_2$. The presence of RuO$_2$ and RuO$_x$ components in the Ru 3d$_{5/2}$ spectrum at 520 K indicates that both phases coexist at this T, P$_\text{O}_2$, P$_\text{CH}_3\text{OH}$ space, the fraction of the RuO$_2$ surface being still dominant. At T ~ 460–480 K the components of the CH$_3$OH-related almost disappear and the O 1s spectra at 520 K have components corresponding to oxide, RuOx and the weakest component at ~531 eV is most likely CO$_x$. At T ≥ 450 K small CO$_x$ and H$_2$O production with almost constant yields in the ~490–520 K range was detected, declining with time at 520 K (see Fig. 1(c)). Apparently under the specific reaction conditions only total oxidation is taking place on the oxide catalyst, which is consistent with the presence of traces of CO$_x$, the only species detected at T > 480–520 K. Most likely the isothermal decline in the CO$_2$ and H$_2$O production at 520 K with time (about 15 min in our experiment) is due to partial reduction of the active RuO$_2$ catalyst surface. The Ru 3d$_{5/2}$ and O 1s spectra evidence that further increase of P$_\text{CH}_3\text{OH}$ to get MMR of 0.25 leads to a very fast reduction of RuO$_2$ into metallic Ru with some adsorbed oxygen. The two spectra in the top panel in Fig. 1(a and b) were measured ~1 (bottom) and 5 min after the P$_\text{CH}_3\text{OH}$ increase. The attained catalyst steady-state under this new MMR condition is characterised by the appearance of a weak surface component in the Ru 3d$_{5/2}$ spectra at 279.5 eV, which indicates that the oxygen coverage drops below 0.5 ML [22], and according to the O 1s spectra these are the only ad-species present under steady conditions. The oxide reduction also changes the catalyst selectivity towards CO, H$_2$ and H$_2$O products, as illustrated by the plots in Fig. 1(c). As can be expected, the dramatic change in the catalyst chemical state from oxide to metal affects the overall catalytic activity as well. Comparing the relative methanol consumption (attenuation mass 31 signal) we evaluated that the conversion of methanol on Ru oxide (MMR = 0.6) is ~8%, whereas on the metal catalyst (MMR = 0.25) it grows to ~29%. Considering the higher P$_\text{CH}_3\text{OH}$ the total number of converted methanol molecules at MMR = 0.25 is about nine times higher.

Very similar reduction of the RuO$_2$ to metallic Ru, which catalyzes the same partial oxidation reaction to CO + H$_2$O + H$_2$ was observed for MMR < 0.5 up to mbar reactant partial pressures (see Fig. 2). However, the increase of the reagent pressures by several orders of magnitude leads to the following expected effects, manifested by the differences in the Ru 3d$_{5/2}$ and O 1s spectra measured at the 10$^{-6}$ and 10$^{-4}$ mbar: (i) the RuO$_2$ catalyst undergoes reduction to metallic Ru at lower temperature (already at ~460 K); (ii) the coverage of the CH$_3$OH and CH$_2$Os species on the oxide precatalyst increases, as judged by the higher intensity of the corresponding O 1s components at ~531.4 and 532.2 eV; (iii) in addition to oxygen the ad-layer at 520 K contains some CO$_x$ indicated by the second component at ~531 eV in the O 1s spectra; (iv) the overall methanol conversion on the metallic Ru in the 10$^{-4}$ range at 520 K and
Fig. 3: (a) Ru 3d\textsubscript{5/2} spectra taken at 470 K (bottom panel) and 720 K (mid panel) showing the evolution of the Ru chemical state at constant $P_{O_2} = 1.2 \times 10^{-4}$ mbar for $P_{CH_3OH} = 2.0 \times 10^{-4}$ (MMR = 0.6) and 0 mbar. The top panel shows the re-oxidation at 720 K with increasing MMR from 0.6 to 3.3 by varying the $P_{O_2}$ and $P_{CH_3OH}$ as indicated in the panel. (b) O 1s spectra corresponding to the Ru 3d\textsubscript{5/2} spectra in the bottom and mid panel of (a). The dashed lines from left to right indicate the O 1s energy positions of CH\textsubscript{2}O\textsubscript{s}, CH\textsubscript{3}O\textsubscript{s}, and OH\textsubscript{s} or CO\textsubscript{s} and the dotted line indicates the oxide component. (c) Normalized mass spectra intensity of reaction products as a function of MMR at 720 K corresponding to the evolution of the Ru 3d\textsubscript{5/2} spectra in the top panel of (a), where $P_{O_2}$ is $2.6 \times 10^{-4}$ mbar and $P_{CH_3OH}$ varies from 2.0 to 0.8 $\times 10^{-4}$ mbar. The arrows indicate the change in the products yield after decreasing the temperature to 600 K.

MMR = 0.3 was ~ 20\%, i.e. considering the $P_{CH_3OH}$ the number of the converted molecules is about 3 orders of magnitude higher compared to almost the same reaction pathway in the $10^{-6}$ range. At the $10^{-3}$ mbar pressure range we also detected very small production of CH\textsubscript{2}O at 520 K (see Fig. 2(c)), indicating that the competing reaction channel to formaldehyde production is opening at high temperatures.

Further-on, we will focus exclusively on the pressure dependence observed for MMR of 0.6, which was found to favour the CH\textsubscript{2}O production in the $10^{-3}$ mbar range, the highest pressures used in our experimental set-up. The Ru 3d\textsubscript{5/2} and O 1s spectra in Fig. 3 shows that in the $10^{-4}$ mbar range the RuO\textsubscript{2} pre-catalyst undergoes partial reduction already at 470 K. The Ru 3d\textsubscript{5/2} and O 1s spectra of the reduced state have the characteristic features of the RuO\textsubscript{x} ‘surface oxide’. In accordance with our previous studies [14] the RuO\textsubscript{2} state cannot be restored at 470 K, but the amount of incorporated oxygen (reflected by the weight of RuO\textsubscript{x} component) can significantly increase after switching-off the CH\textsubscript{3}OH flow. The oxide reduction becomes more efficient at higher temperatures (720 K), as evidenced by the spectra in the mid-panel in Fig. 3(a) and top panel in Fig. 3(b). For the $10^{-4}$ pressure range and MMR = 0.6 the only significant reaction at 470 K and 720 K was the oxide partial reduction to RuO\textsubscript{x} surface oxide state, which is apparently catalytically inactive at these low oxygen and methanol potentials.

The catalyst can be activated in the $10^{-4}$ range if it is reoxidised to RuO\textsubscript{2}, which takes place at temperatures above 600 K by increasing the MMR, as illustrated by the Ru 3d\textsubscript{5/2} spectra in the top panel in Fig. 3(a). However, as expected the steady RuO\textsubscript{2} state at high MMR catalyzes the undesired total oxidation reaction to H\textsubscript{2}O + CO\textsubscript{2}, as shown in Fig. 3(c). At MMR above two very low production of CH\textsubscript{2}O was also detected at 720 K. Reducing stepwise the temperature the H\textsubscript{2}O and CO\textsubscript{2} yields pass through a maximum at 600 K, the CH\textsubscript{2}O yield drops almost to zero (see...

Fig. 4: (a) Ru 3d_{5/2} spectra taken during the CO + O2 reaction illustrating the preserved RuO2 state for reaction temperatures 350–520 K. (b) Normalized CO2 mass spectra intensity as a function of temperature, P_{O2} = 1.6 \times 10^{-4} and P_{CO} = 4.0 \times 10^{-4} mbar.

Fig. 5: Ru 3d_{5/2} (a) and O 1s (b) spectra at different reaction temperatures for MMR = 0.6 at P_{total} = 1.8 \times 10^{-1} mbar. In (a) and dashed lines indicate the RuO2 and RuOx components and the dotted line the bulk metallic Ru. In (b) the dashed lines from left to right indicate the O 1s energy positions of CH2O, CH3O, and OH, or CO2, and the dotted lines the adsorbed oxygen and oxide components. (c) Normalized mass spectra intensity of the reaction products.

the last points in Fig. 3(c) indicated by arrows) and the total methanol conversion increases from 41% at 720 K to 48% at 600 K and MMR = 3.3.

Comparison with the behaviour of the oxidised pre-catalyst during CO oxidation demonstrates the lower stability of the RuO2 state in O2 and CH3OH environment for the sameMMR in the 10^{-4} pressure range. This is due to the release of the very efficient reducing agent H during CH3OH decomposition. The Ru 3d_{5/2} spectra in Fig. 4(a) for reaction temperature from 350 to 520 K show that the oxide catalyst resists reduction down to O2/COMMR of 0.4. As shown in Fig. 4(b) in this temperature range and MMR the RuO2 is very active for CO oxidation with a maximum CO2 yield at 450 K. The decline in the CO2 yield at higher temperatures can tentatively be ascribed to the stability of adsorbed CO and/or cus-oxygen, in fair agreement with the calculated transition temperature, 450 ± 50 K, for O-cus to O-bridge terminated RuO2(110) surface at low pressures [30]. In the case of CH3OH for the same pressure range the RuO2 undergoes partial reduction already at 470 K even in O2-richer mixture. Since the O1s spectra indicated that the steady-state adspecies concentration at T > 450 K is very low (i.e. adsorption–desorption processes of reactant and products is very fast) the different T, P_{O2} stability ranges of RuO2 during CO and CH3OH oxidation is a direct illustration of the stronger effect of methanol chemical potential. This result holds for high pressures as well.

The results in Fig. 5(a and b), obtained for MMR = 0.6 in the 10^{-1} mbar pressure range, show that the oxidised pre-catalyst undergoes similar partial reduction to RuOx as in the 10^{-4} mbar range, but for these reactant’s pressures and T > 470 K the RuOx exhibits the desired catalyst selectivity to the reaction channel CH3OH + ½O2 = CH2O + H2O. The catalyst performance with stepwise increasing temperatures, illustrated in Fig. 5(c) shows that in the temperature range of the on-going
partial reduction (420–470 K) only the products of non-selective oxidative dehydrogenation, H₂O, H₂, CO and CO₂ are detected in the gas phase. After each temperature ramp their yields decayed fast (~2 times) during the isothermal period and the plots in Fig. 5(c) shows the steady mass signal after the decay. The isothermal decay correlates with the changes in the catalyst surface, which according to the Ru 3d₅/₂ and O 1s spectra in Fig. 5(a and b) involve partial reduction and desorption of the CH₂OH-related ad-species. The steady states for the 420–470 K range can be described as coexisting oxide and surface oxide regions with strongly decreased concentration of ad-species. Complete extinction of the oxide component was observed at ~490 K and above this temperature the catalytically active state has only the spectral features of the RuOₓ surface oxide. Above 470 K the yields of the CH₂OH dehydrogenation products (H₂ and CO) drop, whereas the H₂O and CO₂ yields continue growing. The desired product CH₂O appears at ~470 K, the H₂O and CH₂O become the principle reaction products above 500 K and at 540 K the total methanol conversion reaches 28%. The binding energy of the second weak component in the O 1s spectra suggests that under steady conditions at 540 K only very small concentration of CH₃O₅ species is present on the surface.

More light about the origin of the H₂O, H₂, CO₂, and CO₂ yields at temperatures below 480 K is obtained from a ‘TPD-type’ experiment performed at the same reactant pressures, ramping continuously the temperature with 5°/min and monitoring in situ the mass and Ru 3d₅/₂ spectra. The XPS spectra confirm the conversion of the RuO₂ to RuOₓ in the temperature range 420–500 K (Fig. 6(a)). The ‘TPD’-like mass spectra in Fig. 6(b) can result from several competing reactions: recombination of OHs to H₂O + Hs, decomposition of the CH₂Oₓ to CO₂ and Hs and following secondary oxidation of fraction CO and Hs to CO₂ and H₂O, the other CO and Hs fraction desorbing as CO and H₂ in gas phase. The fact that the CO₂ and H₂O maxima are shifted to higher temperature with respect to that of H₂ and COs indicates that H₂O and significant amount of CO₂ are formed via secondary reactions. Another competing viable pathway of CO₂ + H₂O formation is via CH₃H₂Oₓ + Oₓ → H·HCOOₓ + (x-1)H₂ → CO₂ + H₂O, where H₂ can desorb as H₂ or reacts with OHs and desorbs as H₂O. We cannot exclude contribution of this reaction to the mass spectra in Fig. 6, because the classical TPD experiments of methanol adsorption on RuO₂ showed that some CH₃Ox species are present on the surface up to 450 K and can undergo dehydrogenation/oxidation to HCHO₂ according to the scheme above [26,31]. The ‘TPD’ results are also in excellent agreement with the O 1s spectra in Fig. 5, which clearly show that the components related to CH₂Oₓ and OHs species are stable up to 410 K and only some traces of CH₂Oₓ remain at 540 K. As for the experiments in the 10⁻¹ pressure range, in the same temperature range the RuO₂ catalyst undergoes partial reduction, because the reactive desorption of the CH₂Oₓ and OHs species is accompanied by dynamic CH₂OH re-adsorption from the gas phase, as confirmed by the continuous consumption of CH₂OH in the gas phase. Apparently, under the actual reaction conditions the consumption of Oₓ via reactive oxidative desorption of H₂ and CO₂ cannot be compensated by the O₂ adsorption and the oxide catalyst undergoes partial reduction. From the relative attenuation of the mass signal at 31 we evaluated that the conversion of methanol of non-selective oxidation at ~470 K is ~11%, which almost coincides with the consumption measured during step-wise heating ~10%.

4. Discussion

The present results evidence a ‘pressure gap’ in the CH₃OH selective oxidation, which has no simple explanation as in the case of CO oxidation on Ru(0001), where the activation of the metallic catalyst by oxidation is kinetically limited by the low oxygen potentials at PO₂ < 10⁻⁵ mbar. Here, starting with an oxide pre-catalyst we observed significant differences in the selectivity for CH₂OH oxidation at low and high pressures. At given T the reactions depend on the relative methanol and oxygen chemical potentials, which control the catalyst chemical state and adsorbed reactant species. The products of the two non-selective reaction channels, full oxidation to CO₂ + H₂O or partial oxidation to CO + H₂O + H₂ were observed in the whole pressure range considered in the present study, provided the partial reactants pressures and temperatures are properly chosen. Considering the methanol conversion even though measured under significantly different reaction we can conclude that the oxide exhibits high activity for non-selective full oxidation under reaction conditions preserving the RuO₂ surface, high PO₂/PCH₃OH ratio or lower T (see Figs. 1 and 3). Under this conditions desorption of a small fraction of CH₂Oₓ before converting to HCHO₂ or dehydrogenating to COₓ (furter-on HCHO₂, decomposes or CO oxides to CO₂) can occur only at rather high T (720 K), resulting in the traces of CH₂O₂ production. The drop of CH₂O₂ production to zero at 600 K (see Fig. 3) confirms such scenario. Lowering the high PO₂/PCH₃OH ratio affects the stability of the RuO₂ pre-catalyst structure and depending on the actual pressure ratio RuO₂ undergoes partial reduction to a RuOₓ surface oxide or full reduction to metallic Ru. The metallic Ru state catalyzes effectively only non-selective partial oxidation to CO, H₂O and H₂ in the whole pressure range under consideration.

The intriguing result of the present study is that even if the conditions of the low-pressure experiments are selected to attain the same catalytically active chemical state as at high pressures not necessarily the desired reaction is catalyzed at low potentials of the reactants. This concerns the RuOₓ surface oxide state, which becomes active only in the 10⁻¹ mbar range catalyzing the selective oxidation to CH₂O at T > 450 K. As evidenced by the Ru 3d₅/₂ and O 1s spectra in Fig. 5 starting from a RuO₂ pre-catalyst the partial reduction to the RuOₓ surface oxide precedes the onset of selective CH₂O production. The fits of the Ru 3d₅/₂ spectra in Figs. 5 and 6 clearly show that both states, RuO₂ and RuOₓ, coexist in a wide temperature range, which points

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Fig. 6: Evolution of the Ru 3d\textsubscript{5/2} spectra (a) and normalized mass spectra intensity of reaction products (b) monitored during continuous increase of temperature by 5 K/min for MMR = 0.6 at P\textsubscript{total} = 1.2 \times 10\textsuperscript{-1} mbar. The dotted line in (b) shows the attenuation of mass 31, a measure of CH\textsubscript{3}OH conversion.

towards a patchy surface. Above 500 K the RuO\textsubscript{2} component is practically absent and the weight of the RuO\textsubscript{x} component characterises the catalytically active state as a thin few layer surface oxide with poorly defined stoichiometry and structure.

A plausible reason for the observed pressure gap in RuO\textsubscript{x} activity to CH\textsubscript{2}O formation should be kinetic limitations to get the optimal coverage of the reacting species with specific adsorption configurations favouring the CH\textsubscript{2}O production. Undoubtedly, the RuO\textsubscript{2} reduction process involving a massive mass transport and restructuring can result in built-up of strain and/or surface roughening and the degree of such dynamic morphological changes may generate configurations with specific reactivity, related to a specific T, P space. This may also determine the critical amount of incorporated oxygen, which selectively activates the catalyst surface to build the optimum surface coverage of the reacting species for the desired reaction channel. Consequently, the high catalyst selectivity should be observed only in a narrow T, P\textsubscript{O2}, P\textsubscript{CH3OH} space providing the most favourable energetics of interlinked processes of adsorption, desorption, surface diffusion and surface reactions. For the reaction system under consideration the crucial intermediate steps relevant to CH\textsubscript{2}O production are the following:

\[
\begin{align*}
\text{CH}_3\text{OH} + O_s &\rightarrow \text{CH}_3\text{O}_s + \text{OH}_s \\
\text{CH}_3\text{O}_s &\rightarrow \text{CH}_2\text{O}_s + \text{H}_s &\rightarrow \text{CH}_2\text{O}_\text{gas} + \text{H}_s \\
\text{CH}_2\text{O}_s + O_s &\rightarrow \text{HCOO}_s + \text{H}_s \rightarrow \text{CO}_2 + \text{H}_s \\
\text{CH}_2\text{O}_s + O_s &\rightarrow \text{CO}_s + \text{H}_s \text{and/or OH}_s
\end{align*}
\]

In our experiments reaction (2) is slower than (1), which sustains some low concentration of CH\textsubscript{3}O\textsubscript{s}, the only ad-species detected under steady conditions at 540 K. Apparently the catalytically active state should promote reaction (2) with immediate CH\textsubscript{3}O\textsubscript{s} desorption. If the CH\textsubscript{2}O\textsubscript{s} lifetime on the surface is long enough it can undergo further oxidation/dehydrogenation reactions, types (3) and (4), which favour CO\textsubscript{2} or CO pathways. The most plausible explanation is to correlate the selective CH\textsubscript{2}O production to the thermal stability of CH\textsubscript{2}O\textsubscript{x}. CH\textsubscript{2}O\textsubscript{x} can be bonded to the surface in two configurations, single-bonded through the O lone pair orbital, or double-bonded via C and O atoms through carbonyl porbital, the latter being the more stable one [19]. The less stable single-bonded configuration is the preferred one in the presence of oxygen. Therefore one can easily envision that optimal amount of oxygen present at the surface can critically affect the product selectivity not by direct participation in the reaction but via modification of the surface electronic properties and destabilizing adsorbate-adsorbate interactions, which tune the kinetics of CH\textsubscript{2}O desorption.

5. Conclusions

In situ XPS and mass spectrometry shed light on the sensitivity of competing methanol oxidation pathways to the ‘pressure gap’, starting with a Ru oxide pre-catalyst and varying the partial reactants pressure from UHV to mbar range. We found that the three main oxidation channels, namely total oxidation to CO\textsubscript{2} + H\textsubscript{2}O, partial oxidation to CO + H\textsubscript{2}O + H\textsubscript{2} and partial oxidation to CH\textsubscript{2}O + H\textsubscript{2}O, require completely different catalyst chemical states, which develop only under specific T, P\textsubscript{O2}, P\textsubscript{CH3OH} reaction conditions. For all oxygen/ methanol partial pressure ratios used in the present study only the formaldehyde production...

is hindered at low pressures, with exception of some traces detected at $T > 600$ K.

In the whole pressure range under consideration the RuO$_2$ phase is found to be stable only in the O$_2$-rich mixtures and catalyzes the total oxidation to CO$_2$ + H$_2$O. In CH$_3$OH-rich mixtures and $T > 420$ K the RuO$_2$ undergoes reduction even at pressures as low as 10$^{-6}$ mbar and depending on the reactants partial pressures the reduction can terminate at the transient RuO$_x$ surface oxide state. The metallic Ru catalyzes the partial oxidation reaction CO + H$_2$O + H$_2$, which is also pressure insensitive. The RuO$_x$ state turned out to catalyse preferentially the formaldehyde production. Although this state can be formed at low pressures it is activated only at 10$^{-1}$ mbar pressures. Such ‘pressure gap’ in the selectivity was tentatively ascribed to the correlation between oxygen coverage and the lifetime of the CH$_2$O intermediate at the surface, the optimal conditions being determined by a narrow T, P$_{O2}$, P$_{CH3OH}$ space.

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