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Catalytically Active States of Ru(0001) Catalyst in CO Oxidation Reaction

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Abstract

Identifying the composition of the catalytically active state of metal catalysts under dynamic operating conditions is of particular importance for oxidation catalysis. We report here new insights into the chemical identity of different catalytically active states formed on a Ru(0001) catalyst during the CO oxidation at different reaction temperatures. The changes in the surface composition of the Ru catalyst and the CO_2 yield under varying reaction conditions in the 10^{-4} to 10^{-1} mbar pressure range were followed in-situ by synchrotron-based high-pressure x-ray photoelectron spectroscopy and mass spectroscopy. The obtained results reveal that the catalytic activity of a few layers thick 'surface oxide' without well defined stoichiometry and structure is comparable with the activity of the stoichiometric $RuO_2(110)$ phase. The 'surface oxide' forms under reaction conditions when the formation of the RuO_2 is kinetically hindered, and can coexist with RuO_2 in a wide temperature-pressure range.

Keywords: CO oxidation, Ru, high pressure XPS, catalytically active states

1. Introduction

Following the pioneering works demonstrating very high activity of the so-called O-rich Ru(0001) surface in CO oxidation [1,2], the rutile $RuO_2(110)$, formed on the Ru(0001) surface under realistic oxidation conditions, is considered as the catalytically active state [3,4]. The rutile $RuO_2(110)$ surface consists of alternating rows of six-fold and unsaturated five-fold oxygen coordinated Ru atoms, the latter, called cus-Ru, playing a prominent role as active sites in CO oxidation. The inspired UHV surface science and theoretical studies of CO oxidation reaction on a model $RuO_2(110)$ single crystal surface reached the consensus that the elementary reaction steps involve CO and O adsorption on the cus-Ru, followed by reaction between cus-CO and cus- or bridge O atoms [5-9]. However, the $RuO_2(110)$ surface is an idealised case of an active Ru catalyst, which has been prompted by the parallel studies focused on the oxidation mechanism of the Ru(0001) surface and the stability of the Ru oxidation states at different partial pressures and temperatures [10-16]. After the completion of the O-(1x1) adsorption phase [17] , the suggested oxidation pathway of the Ru(0001) surface involves as an important intermediate step the incorporation of O atoms between the first and second Ru layers and the formation of an O_{ad}-Ru-O_{sub} trilayer hosting 2 ML of oxygen [18,19] 1 ML equals the number of Ru atoms on the (0001) surface. The conversion into a $RuO_2(110)$ structure is supposed to occur above the critical thickness of two O-Ru-O trilayers (oxygen content of 4 ML). Spectroscopic evidence for subsurface oxygen species has been provided by photoelectron diffraction and combined photoemission and thermal desorption spectroscopy [20,21] according to another model, based on investigations of Ru oxidation carried out at $T > 600$ K, the RuO_2 nucleus is formed as far as the oxygen exceeds 1 ML, the coverage of the most dense (1x1) adsorption phase, and the $RuO_2(110)$ film grows progressively in autocatalytic manner [10,22].

The recent XPS microscopy and TDS studies demonstrated that starting from an atomically clean Ru(0001) surface, the formation of a stoichiometric RuO_2 phase is kinetically hindered at temperatures lower than 500 K and readily occurs at higher temperatures [2,13,14,21]. The main reason for such temperature dependence of the Ru oxidation state is that the incorporation up to 3 ML of oxygen at T < 500 K is limited to the top 2-3 Ru layers. These O-rich thin films with poorly-defined Ru_xO_y structure are called 'surface oxide' and are identified as the precursor where the RuO_2 nucleates and grows at temperatures above 550K.

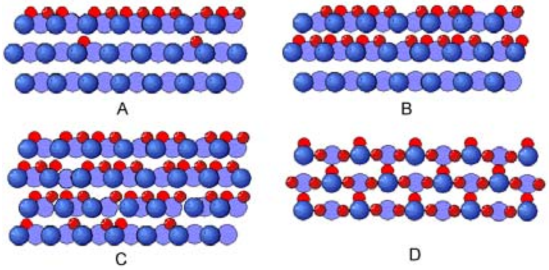

Figure 1: Ball models of the oxidation states of Ru(0001), where O atoms are the red balls. A: (1x1) saturated oxygen adsorption phase with ~1 ML oxygen, the onset of subsurface O incorporation at T ≥ 400 K; B: 'surface oxide' with ~ 1 ML incorporated oxygen, the dominant phase formed at T < 500 K; C: 'surface oxide' with ≥ 2 ML incorporated oxygen; D: rutile $RuO_2(110)$ phase.

Fig. 1 shows schematically the 'oxidation' states of the Ru(0001) that have attained experimental proof [2,4,13,14,21] In the following we will call them: adsorption phase, referring the state when oxygen in present only on the surface with maximum coverage 1 ML (A), 'surface oxide' with ~ 1-3 ML oxygen incorporated within the top few Ru layers (B and C) and rutile RuO_2 phase (D). An important finding of XPS microscopy is that 'surface oxide' and RuO_2 phases coexist in a wide T-pressure range, even when formed in a pure O_2 ambient [13,21] Undoubtedly under reaction conditions, the CO will drive the oxidation state away from the equilibrium achieved in O_2 ambient, which implies that the T-p space of coexistence of the two phases may be expanded.

The temperature dependence of the actual 'oxidation' state and the morphology of the Ru surface reopen the disputable issue about the active state of Ru catalysts during CO oxidation. Here, we utilize a specially built reaction chamber for simultaneous monitoring the chemical state of the catalyst surface and the reaction product released in the gas phase at pressures up to a few mbar. We verified the catalytic activity of the different oxidation states of Ru(0001) catalyst, including the final stoichiometric RuO_2, starting from a metallic Ru surface and following in-situ the temperature evolution of the catalyst surface composition in CO+O_2 environment close to the realistic oxidation, reduction and steady-state reaction conditions.

2. Experimental

The experiments were performed in the high pressure XPS station designed and constructed in FHI-MPG [23], attached to the beamline U49/2-PGM2 at the synchrotron radiation facility BESSY in Berlin. The overall energy resolution of the beamline was 0.1 eV at 500 eV. The photoelectron spectra were measured in-situ using a set-up combining differential pumping and electrostatic focussing of the emitted photoelectrons [24]. Briefly, the sample was mounted inside the reaction cell, 2 mm away from an aperture (1 mm diameter), which was the entrance of the emitted photoelectrons and reaction products to the differentially pumped stages of the electrostatic lens system of the hemispherical analyser Phoibos 150 (SPECS GmbH). The gas phase products, used to measure of the catalytic activity, were monitored on-line by a Hiden mass spectrometer located in the first differentially pumped lens stage. The sample was heated by a laser from the backside. The CO and O_2 gas flows into the reaction cell were regulated by leak valves.

The Ru(0001) sample was cleaned before each reaction cycle using the well established procedures [14,25]. The base pressure in the chamber was ~ $2x10^{-8}$ mbar, which reduced the lifetime of the atomically clean surface at room temperature. The temperature ramp used in the present studies was 2 K per min, and the acquisition of a set of Ru 3d and O 1s spectra required maximum 4 min. Thus, the maximum difference between the temperature at which the Ru 3d and O 1s spectra were taken was less than 8 K. All spectra were normalized to the incident photon flux, monitored by a photodiode with known quantum efficiency. The Ru 3d and O 1s spectra were measured with photon energies 450 eV and 650 eV, respectively. Using the universal curve for the electron mean free path [26] the effective escape depths for the O 1s and Ru 3d photoelectrons is ~ 5 Å, which limits the probing depth to the top few layers (~ 10 Å). We also used higher photon energies for increasing the probing depth when necessary.

3. Results and discussion

The experiments were carried out at different partial pressure ratios of CO and O_2 in the range between 10^{-4} and 0.1 mbar. By varying the CO/O_2 pressure ratio it was possible to reproduce oxidation, reduction and steady-state conditions of the working Ru catalyst. Simultaneous monitoring the dynamic response of the O 1s and Ru $3d_{5/2}$ core level spectra and the CO_2 production allowed us to correlate the catalytic activity to the actual oxidation state of the Ru catalyst.

The necessary basis for identification of the adsorption, 'surface oxide' and RuO_2 states and verify their actual role in CO oxidation reaction was provided by the already available Ru $3d_{5/2}$ and O 1s core level and TD spectroscopy data. The established binding energies of the Ru $3d_{5/2}$ and O 1s components corresponding to the adsorption state, 'surface oxide' states and rutile RuO_2 phase are summarized in Table I.

Table 1: Energy positions of Ru $3d_{5/2}$ and O 1s components measured for the different oxidation states. The shift of the Ru $3d_{5/2}$ components with respect to the zero-energy reference (the position of the Ru $3d_{5/2}$ bulk component at 280.1 eV) is given in the brackets.

State	Binding Energy (eV)	Component	Ref.
Clean Ru	280.1 (0)	Ru_{bulk}	25
	279.75 (-0.35)	Ru(I)	25
	280.25 (0.15)	Ru(II)	25
Adsorbed	280.08	Ru(I)-$1O_{ad}$	25
phase	280.48 (0.4)	Ru(I)-$2O_{ad}$	4, 25
	281.03 (0.93)	Ru(I)-$3O_{ad}$	4, 25
RuO_2	280.74 (0.64)	RuO_2-bulk	4,13,
phase	280.45 (0.35)	Ru-cus	27
	283 (2.92)	satellite	
'surface	280.5±0.05 (~0.4)	Ru_xO_y	21
oxide'	280.6±0.05 (~0.8)	Ru(I)-$2O_{ad}O_{sub}$	21
	281.4±0.05 (~1.3)	Ru(I)-$3O_{ad}O_{sub}$	21
	280.9±0.05 (~0.5)	Ru(II)-O_{sub}	21
	530.0	O_{ad}&O_{sub}	13
O1s	529.5	O in RuO_2-bulk	4, 13
	528.7	'bridge' O	4
O1s-CO	530.8-531.8		28

The Ru(I) and Ru(II) components account for emission from the Ru atoms in the first and second layer, respectively. They undergo distinct chemical shifts when binding to O, determined by the coordination number of O atoms and their bonding configuration [4,25]. The incorporation of O subsurface, O_{sub}, leads to a distinct shift of Ru(II) resulting in the component Ru(II)-O_{sub} at ~ 0.5 eV, well separated from the Ru_{bulk} position [21]. The Ru(I) energy shift induced by the subsurface oxygen accounts for the Ru(I)-$2O_{ad}O_{sub}$ and Ru(I)-$3O_{ad}O_{sub}$ components at ~0.8 and 1.3 eV, assigned to Ru(I) atom coordinated with 2 or 3 O adatoms, respectively, and subsurface oxygen below. When the total amount of adsorbed and incorporated oxygen exceeds ~ 3 ML a new broad component at ~ 0.4 eV, Ru_xO_y, grows. It corresponds to the most advanced oxidation state below 500 K with a poorly-defined structure and thickness of about two rutile layers (5-6 Å) [21]. Although the energy position of the Ru_xO_y component is practically identical with the Ru(I)-$2O_{ad}$ one, the Ru 3d spectra are very different, because of the strong attenuation of Ru_{bulk} component due to screening by the 'surface oxide' film. The $RuO_2(110)$ phase has two components corresponding to the cus-Ru and six-fold coordinated Ru atoms and a broad satellite at ≈ 283 eV [4,13,27]. The O 1s spectra from the adsorption and 'surface oxide' states appear at 530.0 eV, the latter being only a bit broader, indicative of multiple bonding configurations [13]. The O 1s spectrum of the $RuO_2(110)$ phase has two components, reflecting the emission from the bridge-O atoms at the RuO_2 surface (528.7 eV) and bulk RuO_2 oxygen (529.5 eV) [4,13]. The 'bridge' oxygen component is well visible only when the $RuO_2(110)$ surface is very well ordered and without oxygen vacancies. Since the 'bridge' oxygen participates in the oxidation reactions [9,10] the corresponding O 1s component should be strongly reduced in CO ambient.

For the presence of adsorbed CO we judged from the O 1s spectra, because the C 1s peak overlaps with the Ru $3d_{3/2}$ core level. The O 1s peaks of CO have binding energies between 530.8 and 531.8 eV and can be easily resolved from those of adsorbed oxygen and oxide [28].

3.1 Reduction of the 'surface oxide' and RuO_2

The 'surface oxide' (Fig. 2) and stoichiometric RuO_2 phase (Fig. 3) were formed by exposing Ru(0001) to $5x10^{-2}$ mbar O_2 at 450 K and 620 K, respectively. The 'surface oxide' contained ~ 1.5-2.0 ML oxygen located on the surface and between the top and second Ru layer. The experiments were carried out in the 10^{-4} mbar range at CO/O_2 partial pressure ratio of 4, i.e. in excess of CO. The reduction rate was compatible with simultaneous monitoring of the XPS and mass spectra, while slowly increasing the sample temperature, starting from 370 K. The results provide the necessary basis for understanding and interpretation the in-situ CO oxidation data.

Figure 2(a) shows representative Ru $3d_{5/2}$ spectra obtained during reduction of 'surface oxide'. The bottom Ru $3d_{5/2}$ spectrum is of a 'clean' Ru surface, before exposure to $1x10^{-2}$ mbar O_2 at 450 K. Although some CO from residual gas adsorbs on the surface at $2x10^{-8}$ mbar base pressure, its coverage is relatively low at 450 K and the surface component Ru(I) is still present. For deconvolution we used a broader component to account for the bulk and Ru(II) contributions. The Ru $3d_{5/2}$ spectrum of the 'surface oxide' before the reaction contains components at ~ 0.5 eV, 0.8 eV and at 1.3 eV, which appear only in the presence of about 1 ML incorporated oxygen [21]. Our previous XPS microscopy results did not show significant lateral inhomogeneity for such low temperature oxidation states [21]. The broad O 1s spectrum in the bottom Fig. 2(b), peaked at 530.0 eV, corresponds to the 'surface oxide'.

The onset of reduction was at ~ 390 K with a maximum CO_2 yield at ~ 420 K, followed by a fast decay to zero at ~ 450-470 K. It leads to a decrease of the O 1s signal (Fig. 2(c)) and significant changes in the Ru $3d_{5/2}$ spectrum: the Ru_{bulk} grows, accompanied by fast attenuation of the Ru(I)-2$O_{ad}O_{sub}$ at 0.8 eV, whereas the Ru(II)-O_{sub} at 0.5 eV broadens and gradually shifts to 0.4 eV, the position of the Ru(I)-2O_{ad} component. The results indicate that once the oxygen from the surface is consumed, the limited amount of oxygen incorporated between the first and second layer is thermodynamically driven to segregate to the surface [18]. Thus the system converts into an oxygen adsorption phase. A peculiar feature in the evolution of the Ru $3d_{5/2}$ spectra is that the Ru(I)-3O_{ad} component at 0.9 eV does not gain sensible intensity, which indicates direct reduction of the 'surface oxide' into an adsorption state with moderate oxygen coverage of ~ 0.7 ML.

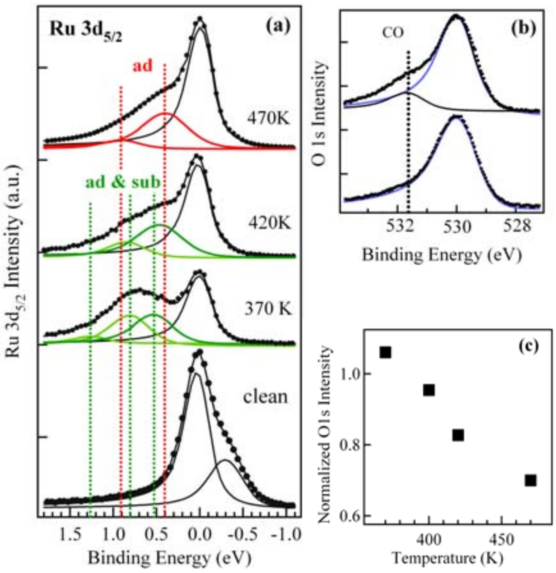

Figure 2: (a) From bottom to top: Ru $3d_{5/2}$ spectra taken before exposure to O_2, after oxidation at 450 K and cooling the 'surface oxide' to 370 K and following reduction with increasing the temperature. The 'ad & sub' annotation indicates the three components, Ru(I)-3$O_{ad}O_{sub}$, Ru(I)-2$O_{ad}O_{sub}$ and Ru(II)-O_{sub}, which are fingerprints of the O-rich state with incorporated oxygen. (b) O 1s spectra taken after oxidation at 450 K (bottom) and after exposure of this surface to CO at 320 K (top). (c) O 1s intensity as a function of reduction temperature. The O 1s signal is normalised assuming that the intensity of the adsorption phase corresponds to 0.7 ML. dT/dt = 2 deg/min. Reduction conditions: $P_{CO} = 2x10^{-4}$ mbar, $P_{O2} = 0.5x10^{-4}$ mbar.

Simple calculations, considering the electron escape depth for our experimental set-up, will predict that for 'surface oxide' with initial load of 2 ML the reduction to 0.7 ML adsorption phase should cause a decrease of the O 1s intensity by ~ 50% (1 ML subsurface oxygen contributes to ~ 30% of the initial signal). The experimentally measured decrease of the O 1s intensity by about 35% is indicative that the total initial load of oxygen within the top two Ru layers is somewhat less than 2 ML. In fact, the Ru(I)-3$O_{ad}O_{sub}$ component at ~ 1.3 eV is already rather weak in the Ru $3d_{5/2}$ spectra from the 'surface oxide' before the reduction, compatible with the presence of vacancies on the surface. This also is consistent with the evolution of the Ru $3d_{5/2}$ spectra during the reduction, which does not pass through a saturated adsorption layer of 1 ML. One possible explanation is that once the oxygen starts to incorporate below the surface it naturally leaves vacancies on the surface [18,29], where CO can stick and react. Indeed, when the freshly formed 'surface oxide was cooled to 370 K and exposed to CO ambient a shoulder at about 531.7 eV grows in the O 1s spectrum due to adsorption of CO molecules (Fig. 2(b)). By varying the CO/O pressure ratio the initial 'surface oxide' can be restored under oxidizing conditions at 450 K, whereas under reducing conditions the adsorbed O can be further depleted only at temperatures above 600 K, which leaves a diluted adsorption state with mostly single coordinated Ru atoms.

The Ru $3d_{5/2}$ spectrum after oxidation in 10^{-2} mbar O_2 at 620 K (Fig. 3(a)) did not contain a Ru_{bulk} component, even when measured using photon energies of 1000 eV, which increased the probing depth. This indicates that the formed stoichiometric RuO_2 film is thicker than ~ 15 Å. The bulk oxide component dominates the spectra but also the Ru-cus component is present, which suggests an uniform and structured $RuO_2(110)$ surface. The O 1s spectrum in Fig. 3(b) is peaked at 529.5 eV, as expected for the RuO_2 phase, with broadening on the side of the O-bridge surface component at 528.7 eV [4,13].

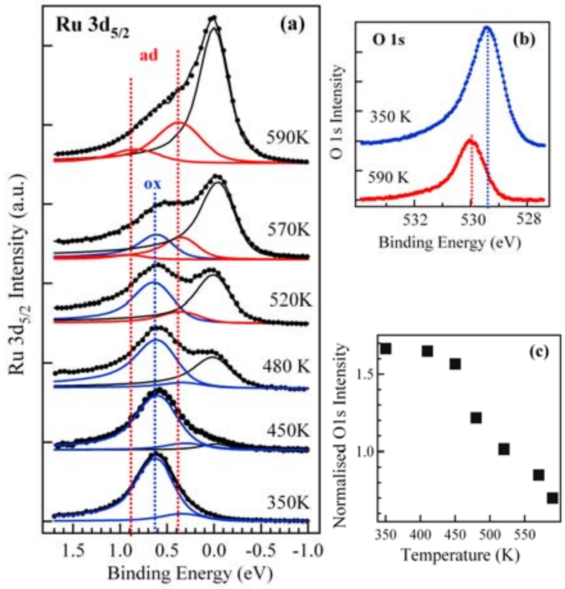

Figure 3: (a) From bottom to top: Ru $3d_{5/2}$ spectra taken after oxidation at 620 K and cooling to 350 K, and following reduction with increasing the temperature. (b) O 1s spectra taken before introducing CO (top) and after reduction to adsorption phase (bottom) (c) O 1s intensity changes with increasing the reduction temperature. The O 1s signal is normalised against the intensity of the adsorption phase, corresponding to 0.7 ML. dT/dt = 2 K/min. Reduction conditions: $P_{CO} = 2x10^{-4}$ mbar, $P_{O2} = 0.5x10^{-4}$ mbar.

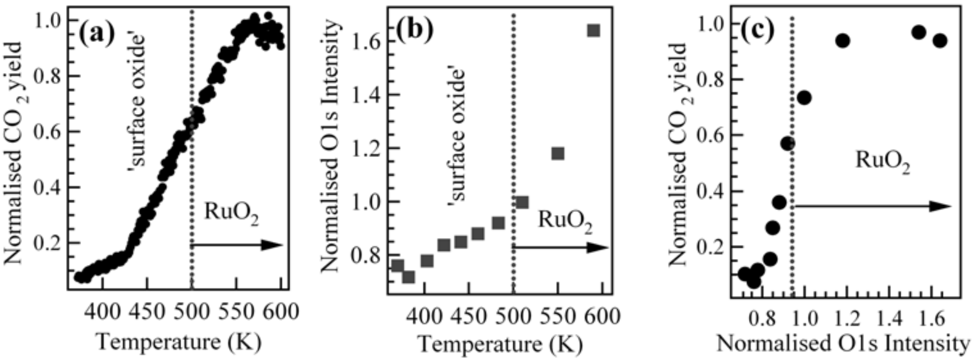

Figure 4: (a) CO_2 yield as a function of reaction temperature; (b) O 1s intensity after subtraction of the CO contribution as a function of reaction temperature. The O 1s signal is normalised as in the reduction experiments (see Figs. 3(b) and 2(b)). The O 1s intensity up to ~ 500 K reflects only the surface and subsurface content, whereas above 500 K the increase is dominated by the formation of an RuO_2 phase. (c) Plot of the CO_2 yield versus O content at the surface and near surface region. The dashed line in (a) - (c) indicates the onset of the RuO_2 growth.

The CO_2 formation starts at ~ 420 K and is clearly marked by the appearance and growth of the Ru_{bulk} compo nent with increasing reaction temperature and decrease of the O 1s intensity. As illustrated by the plot in Fig. 3(c), the most rapid loss of O 1s intensity occurs at ~ 450-470 K, when the maximum CO_2 yield was monitored. The evolution of the Ru $3d_{5/2}$ spectra in Fig. 3(a) illustrates how the on-going reaction continuously consumes the oxide. Above ~ 520 K the Ru(I)-$2O_{ad}$ component starts to grow as well, accompanied by an accelerated increase of the Ru_{bulk} and attenuation of the oxide component. This indicates a patchy morphology of the surface, consisting of diminishing oxide islands and inactive adsorption phase. Above ~ 580 K the Ru $3d_{5/2}$ spectrum becomes almost identical to that of the inactive adsorption state with ~ 0.7 ML of oxygen, achieved during reduction of the 'surface oxide' (see Fig. 2(a)). The apparent direct conversion from RuO_2 to an inactive adsorption phase is supported by the evolution of the RuO_2 satellite (not shown), distinguishable in the Ru 3d spectra up to ~ 550 K. This is consistent with the results in Fig. 2, which show that the 'surface oxide' is unstable at T > 500 K under reduction conditions, and the shift of the O 1s spectrum in Fig. 3(b) to 530.0 eV.

In brief, the stabilities of the 'surface oxide' and the stoichiometric RuO_2 under reduction condition appear comparable; both can be easily reduced in excess of CO in the gas phase mixture at T > 400 K and the final reduced state at T < 600 K is the same inactive adsorption phase with ~ 0.7 ML of oxygen. It should be noted that in surface science experiments, carried out at temperature and pressure conditions far from the realistic ones, no reduction of the $RuO_2(110)$ was observed even in extreme excess of CO, i.e. CO:O_2 pressure ratios of 10 [7].

3.2. Catalytically active transient states of Ru surface during CO oxidation at different temperatures

The experiments were carried out at 0.1 mbar with CO: O_2 partial pressure ratio 1. We started from a clean Ru(0001) surface slowly increasing the temperature after introduction of the reactants in the gas phase. The excess of oxygen with respect to the reaction stoichiometry provided slightly oxidizing conditions in order to ensure the formation of stoichiometric RuO_2 above 500 K, which did not readily occur using the stoichiometric CO:O_2 ratio of 2. Another reason for choosing this CO:O_2 ratio is that the highest turnover rates over working Ru catalysts under realistic conditions were measured at about equal partial pressures of the reactants [30].

The mass spectrometry and XPS data allowed us to correlate the CO_2 yield and the oxidation state of the catalyst at different reaction temperature, ranging from 370 to 600 K. Figure 4(a) shows the evolution of the CO_2 yield with increasing reaction temperature. The plot has three distinct regions: a very weak increase up to ~ 420 K, a sharp onset of the oxidation reaction at ~ 420 K with the CO_2 yield continuously increasing up to ~ 550 K, followed by a flat maximum and slow decline above ~ 580 K.

The evolution of the Ru oxidation state with increasing reaction temperature is illustrated by the selected O 1s and Ru $3d_{5/2}$ spectra in Fig. 5 (a, b). The surface composition of Ru catalyst in the CO+O_2 ambient at temperatures before the sharp onset of the CO_2 production is best represented by the O 1s spectra in Fig. 5(a), taken at T < 420 K. They clearly show the presence of CO on the surface (component at ~ 531.7 eV) up to temperatures ~ 400 K. The CO removal in the temperature range 400-420 K is accompanied by some loss of the O 1s intensity at 530.0 eV, assigned to surface and subsurface oxygen, and by a weak increase of the CO_2 yield. This suggests that the adsorbed CO reacts with surface O and leaves the surface as CO_2.

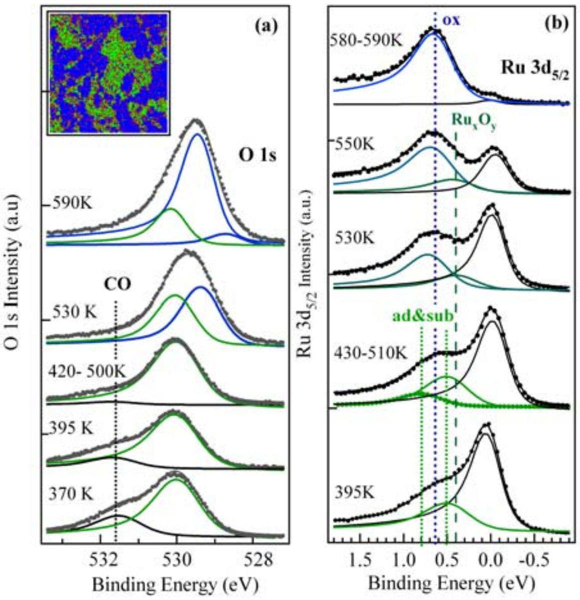

Figure 5: O1s (a) and Ru $3d_{5/2}$ (b) spectra illustrating the catalyst composition developed during CO oxidation with increasing of the reaction temperature from 370 to 600 K. dT/dt = 2 K/min. Reaction conditions: $P_{CO} = 0.5x10^{-1}$ mbar, $P_{O2} = 0.5x10^{-1}$ mbar. The insert in (a) is a Ru 3d map illustrating the surface morphology developed after exposure to 10^6 L O_2 at 670 K with RuO_2 (blue) and Ru_xO_y (green) islands [31]

This scenario is in accordance with the Ru $3d_{5/2}$ spectrum in Fig. 5(b) taken at 395 K, where the absence of Ru(I)-$2O_{ad}O_{sub}$ component indicates that the O surface coverage is substantially reduced after the removal of CO. We did not consider here the Ru $3d_{5/2}$ spectrum before the removal of CO, because of the unknown effect of the CO on the surface core level position. The O 1s peak at 530.0 eV gains intensity above 400 K indicating further accumulation of oxygen, which also leads to the increase of Ru(II)-O_{sub} and Ru(I)-$2O_{ad}O_{sub}$ components in the Ru $3d_{5/2}$ spectra. The Ru $3d_{5/2}$ and O 1s spectra undergo negligible lineshape changes in the temperature range 420-500 K, despite the continuous increase of the CO_2 yield. The deconvoluted Ru $3d_{5/2}$ spectra have a dominant Ru(II)-O_{sub} component at 0.5 eV and a rather weak Ru(I)-$2O_{ad}O_{sub}$ component at 0.8 eV. This means that under the actual operational conditions the catalyst contains a significant amount of subsurface oxygen, whereas the O species on the surface are effectively consumed by the on-going reaction. The fast dynamics at the surface is confirmed by the practical absence of CO-related feature in the O 1s spectra, indicating a short lifetime of the CO species on the surface before being reacted-off.

Since the CO_2 formation reaction cannot disturb significantly the surface composition, the observed temperature dependence of the reaction rate is most likely related to further accumulation of oxygen, facilitated at higher temperature. This accounts for the slow gradual increase of the O 1s intensity below 500 K, as illustrated in Fig. 4(b). In this context we note that the lattice stress induced by incorporation of O changes locally both the geometric and electronic structure of the top Ru layer [18,32], thereby affecting the Ru-O and Ru-CO adsorption bond and/or modifying the adsorbate bonding configurations. As a result the barrier to achieve the transition CO---O state may be reduced, increasing the surface activity and the CO_2 yield.

A natural consequence of the progressive incorporation of oxygen with further increasing the reaction temperature is the nucleation and growth of stoichiometric RuO_2. Indeed, the Ru $3d_{5/2}$ spectra in Fig. 5(b) undergo significant changes above 500 K, due to formation of RuO_2 until a 'steady-state' composition is reached and maintained in the 550-600 K range. A weak Ru_{bulk} component can still be distinguished in the Ru $3d_{5/2}$ spectrum of this 'steady-state', compared to much thicker RuO_2 films grown in pure O_2 ambient (see Fig. 3(a)). This indicates that the RuO_2 growth during CO oxidation is slower, reflecting the kinetic limitations imposed by the presence of CO. Considering our XPS microscopy findings [13] the hindered oxide growth should result in a patchy structure consisting of RuO_2 islands and Ru_xO_y areas, the latter accounting for the presence of the Ru_{bulk} component. A typical morphology of such surface is illustrated by the Ru $3d_{5/2}$ image in the O 1s panel in Fig. 5(a). The RuO_2 islands appear dark (blue), because the RuO_2 phase contains less Ru atoms per unit volume than the adsorption and O-rich intermediate states (green) and also being thicker it screens more effectively the emission from the metallic Ru below. Similar coexistence of the two phases was observed in very wide temperature (600-775 K) and exposure range [13,21]. Since the Ru_xO_y component appears close to the cus-Ru component of the $RuO_2(110)$ surface (see Table I), and it is speculative to fit the Ru $3d_{5/2}$ spectra using three components with unknown weight we allowed a broadening of the dominant oxide component at ~0.6 eV to account for all contributions. The coexistence of the both oxidation states is confirmed by the corresponding O 1s spectrum, which contains the 'surface oxide' and RuO_2 components. Judging from the relative weight of the 'surface oxide' O 1s component, about 80% of the surface should be covered with RuO_2 islands at 590 K. Note that the RuO_2 bridge-O component at 528.7 eV is very weak, probably due to its continuous consumption during the reaction, in accordance with the mechanism suggested in ref. 7, 9. The reaction rate can be reverted back and forth by decreasing-increasing the temperature in the range 550-600 K, which does not affect visibly the catalyst surface composition.

The most striking result is that the growth of the RuO_2 phase above 500 K does not affect the monotonous increase of the CO_2 yield (Fig. 4(a)). This suggests that the nucleation and growth of a stoichiometric oxide phase barely affects the reaction barrier. The plot of the CO_2 yield vs O content in Fig. 4(c) is the best illustration that the high catalytic activity of the Ru catalyst is not exceptionally correlated to the formation of RuO_2 with a well defined surface structure. It clearly shows that the 'surface oxide' formed via progressive incorporation of oxygen already exhibits high catalytic activity and there is no significant increase with the formation of stoichiometric RuO_2. Here, it should be noted that since the formation of RuO_2 occurs above 500 K, when comparing the catalytic activity of the 'surface oxide' and RuO_2 the positive temperature effect on the reaction rate should be taken into account as well.

The evidenced coexistence of 'surface oxide' and RuO_2 states does not allow obtaining unambiguous results correlating the CO_2 yield to a single phase by running the reaction at a constant temperature above 500 K, when the nucleation and growth of the RuO_2 takes place. However, the catalytic activity of the 'surface oxide' was confirmed by recent experiments performed using the stoichiometric $CO:O_2$ partial pressure ratio of 2, instead of 1, keeping the same total pressure of 0.1 mbar. We increased the temperature from 400 to 600 K in steps of 20-25 degrees, waiting at each temperature until the CO_2 signal reaches a constant value. In this case the higher $CO:O_2$ gas pressure ratio hindered the formation of the RuO_2 state. It was evidenced by the evolution of the Ru 3d and O 1s spectra, which was terminated at the formation of 'surface oxide'. The CO_2 yield grew steadily showing stable activity at constant temperature until levelling off at around 500 K and declining slowly above 550 K. This result is qualitative agreement with the results with powdered Ru catalyst which demonstrate that an ultra-thin oxide layer covering the metallic Ru core is the active state in CO oxidation at temperatures below 500 K [33].

4. Concluding remarks

The in-situ capability of high-pressure photoelectron spectroscopy has provided real-time information about the evolution of chemical state of Ru(0001) catalyst during CO oxidation with increasing reaction temperature. The results confirm that the metallic state of Ru is inactive. The most important finding is that the CO_2 production is not phase selective, i.e. there is no distinct difference between the catalytic activity of the stochiometric $RuO_2(110)$ and a few layers thick not well-ordered 'surface oxide'.

According to the DFT predictions the higher catalytic activity of an oxide surface, compared to the corresponding metal surface, is not only due to the weaker CO and O bonding on the oxide; an important and in some cases even decisive role is the reorganisation required to achieve the configuration of the transition state [16]. In the frame of this concept the activation role of the subsurface oxygen should be ascribed to the induced deformation of the lattice, which affects the O and CO adsorption configurations. The growth of stoichiometric RuO_2 does not change substantially the reaction barrier. This result is not surprising, because, as noted above, the activity is determined by the O and CO bonding configurations on the catalyst surface. Apparently, the amorphous surface oxide formed below 500 K has attained a favourable structure with activity comparable to that exhibited by the well-defined RuO_2 phase formed at higher temperatures.

In excess of CO the limited amount of subsurface oxygen is energetically driven to segregate to the surface and the amorphous 'surface oxide' can easily lose the incorporated oxygen and convert into an inactive adsorption phase. However, the RuO_2 also is unstable in excess of CO and similarly to the 'surface oxide' can be reduced into an inactive adsorption phase but it is not necessary to reoxidise back the reduced catalyst to the initial stoichiometric RuO_2 in order to regain catalytic activity.

The surface phase diagram of the $RuO_2(110)$ surface, reported in ref. 6, considers that the catalytically active region under realistic dynamic reaction conditions can often lie at the boundary between two phases. The present study provides experimental evidence that the highest CO oxidation rate is monitored in the temperature range 500 – 600 K, when two Ru oxidation states coexist.

The results in this work apply well to real Ru catalyst systems, which are nano-particles forming amorphous oxide with not well-defined stoichiometry [34,35]. Such 'oxidized' states of the Ru nanoparticles, often described as Ru_xO_y, are comparable to the 'surface oxide' with subsurface oxygen rather than with the well-structured $RuO_2(110)$ surface. We confirm in this study that the RuO_2 formed at temperatures above 500 K is also active, but represents a limiting case of a well-ordered model structure. The long-range ordering of the $RuO_2(110)$ surface is not prerequisite for catalytic function but was instrument to unravel and theoretically understand mechanisms of CO oxidation at the atomic level. As noted above, very recent study of the CO oxidation on polycrystalline powdered Ru catalyst in the temperature range 363-453 K showed that under dynamic catalytic conditions the active state are the ultra-thin Ru oxide films, whereas fully oxidized RuO_2 particles, formed at higher temperature, exhibit lower activity [33]. This deactivation is tentatively attributed to roughening and formation of inactive RuO_2 facets.

In general, the long-range ordered oxide structures available in macroscopic systems can not be the ones working under conditions of high chemical potential and enabled structural dynamics ("real world"). However, they are excellent model systems for fundamental experimental and theoretical studies of catalytic reactions. They help identifying the general reactivity trend on metallic and O-rich states of catalysts used in redox processes.

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