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

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1. Introdiction

The recent XPS microscopy and TDS studies clearly showed that the formation of a rutile RuO_2 phase, starting from an atomically clean Ru(0001) surface, is kinetically hindered at temperatures lower than 500 K and readily occurs at temperatures higher than 550 K[1]. An important finding is that 'surface oxide', which forms by incorporation of O atoms below the top Ru layer and the RuO_2 can coexist in a wide T-pressure range, even when formed in pure O_2 ambient[2]. Undoubtedly, when CO oxidation reaction takes place, 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 structures may be expanded. The temperature dependence of the actual 'oxidation' state and the complex morphology of the Ru surface evidenced by XPS microscopy have reopen the disputable issue about the active state of Ru catalysts during CO oxidation[3,4,5].

We verified the catalytic activity of the different oxidation states of Ru(0001) catalyst, starting from a metallic Ru surface and following in-situ the temperature evolution of the catalyst surface composition and yield of CO_2 during CO oxidation reaction carried out close to the realistic reaction conditions.

2. Experimental

The experiments were performed in the high pressure XPS station designed and constructed in FHI-MPG, attached to the beamline U49/2-PGM2 at BESSY[6]. The XPS spectra, were measured in-situ using a set-up combining differential pumping and electrostatic focusing of the emitted photoelectrons and simultaneously the CO_2 yield was monitored by a mass spectrometer. The Ru(0001) sample was cleaned before each reaction cycle using the well established procedures of alternating Ar ion bombardment and oxidation-annealing cycles. Photon energies 450 eV and 650 eV were used for monitoring the Ru 3d and O 1s spectra, respectively.

3. Results

The dynamic response of the O 1s and Ru $3d_{5/2}$ core level spectra was used for precise assignment of the catalyst oxidation state in the course of the reaction correlated to the corresponding CO_2 yield. The already available Ru $3d_{5/2}$ and O 1s core level spectroscopy data provided the necessary basis for identification of the adsorption, 'surface oxide' with incorporated oxygen, and stoichiometric RuO_2 states and verifying their actual role in CO oxidation reaction[1,7]. We started from a clean Ru(0001) surface and followed the changes after introducing 0.1 mbar CO+O_2 (O_2:CO partial pressure ratio 1) and slowly increasing the temperature. The excess of oxygen with respect to the reaction stoichiometry provided slightly oxidizing conditions ensuring the formation of the different Ru oxidation states.

Fig. 1 (a) shows the CO_2 yield as a function of the reaction temperature. There is a clear sharp onset of the reaction at ~ 420 K, the reaction rate increasing continuously in the temperature range 420-500 K. The selected set of Ru $3d_{5/2}$ and O 1s spectra in Fig. 2, measured at different reaction temperatures, represent the milestones in the evolution of the catalyst

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oxidation state. The first Ru $3d_{5/2}$ and O 1s spectra represent the status of the Ru catalyst after the onset of CO_2 production. The Ru $3d_{5/2}$ spectra of this 'low temperature' state require the characteristic components of the 'surface oxide', Ru(II)-O_{sub} and Ru(I)-$2O_{ad}O_{sub}$, where Ru(I) and Ru(II) account for emission from the Ru atoms in the 1st and 2nd layer, bonded to oxygen residing on the surface, O_{ad}, and below the surface, O_{sub}[1]. The Ru $3d_{5/2}$ and O 1s spectra undergo negligible lineshape changes in the temperature range 420-480 K despite the gradual increase of the CO_2 yield. They resemble those measured for the 'surface oxide' with ~ 2 ML oxygen, but with less oxygen on the surface (the Ru(II)-O_{sub} component at 0.5 eV is dominant). Apparently the adsorbed oxygen is kept low, since it is very effectively consumed by the on-going reaction. The very fast dynamics at the surface is confirmed by the absence of a CO-related feature in the O 1s spectra at binding energy > 531.0 eV (Fig.2), indicating that the lifetime of the CO on the surface before being reacted is shorter than that of the O species.
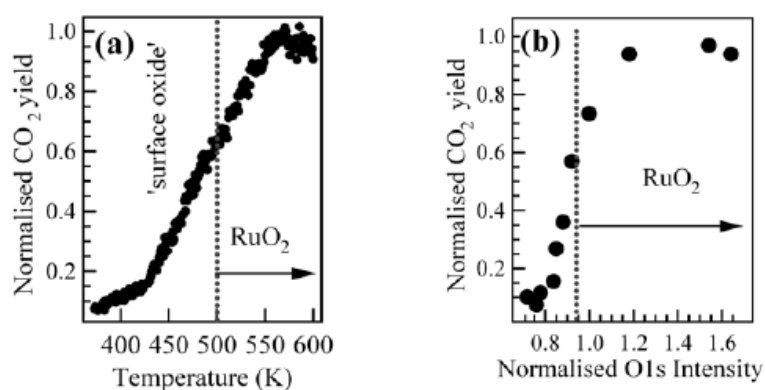

Fig. 1 (a) CO_2 yield as a function of reaction temperature. (b) Plot of the CO_2 yield versus O content at the surface and near surface region. The dashed line in (a) - (c) indicates the onset of the RuO_2 growth.

Natural consequence of the progressive incorporation of oxygen with further increasing the reaction temperature is the nucleation and growth of stoichiometric RuO_2. This is manifested by the significant changes of the Ru $3d_{5/2}$ spectra in Fig. 2 undergone above 500 K, until a 'steady-state' composition is reached and maintained in the 550-600 K range, when the 'oxide' component is dominant in the Ru $3d_{5/2}$ spectra. Ru_{bulk} component can still be distinguished in the Ru $3d_{5/2}$ spectrum of this 'steady-state' as well as the O1s component corresponding to the 'surface oxide'. This indicates a patchy structure consisting of RuO_2 islands and 'surface oxide' areas, as reported in ref. 2, reflecting the kinetic limitations imposed by the presence of CO.

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. 1(a)), suggesting that the nucleation and growth of the oxide phase barely affects the reaction barrier. The plot of the CO_2 yield vs O content in Fig. 1(b) 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 the temperature effect on the reaction rate should be also taken into account when comparing the catalytic activity of the 'surface oxide' and RuO_2.

4. Concluding remarks

The present results demonstrate that one cannot draw a clear line between the catalytical activity of the stoichiometric RuO_2 phase and a few layers thick not well-ordered 'surface oxide'. Our findings are in qualitative agreement with the theoretical predictions[8] that the

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catalytically active region under realistic dynamic reaction conditions can often lie at the boundary between two structures. Present results also apply well to real Ru catalyst systems which are nano-particles. The 'oxidized' states of these Ru nanoparticles, often described as Ru_xO_y or ultra-thin Ru oxide films covering the metallic core, are comparable to the 'surface oxide' with subsurface oxygen rather than with the well-structured $RuO_2(110)$ surface[9,10].
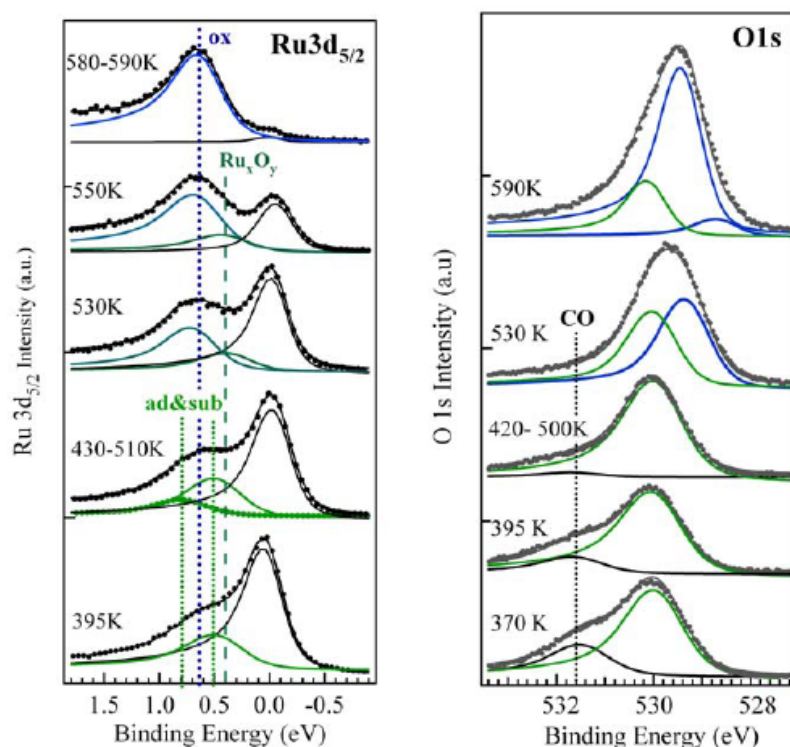

Fig. 2. Ru $3d_{5/2}$ and O 1s spectra illustrating the catalyst composition developed during CO oxidation with increasing of the reaction temperature from 370 to 600 K. dT/dt = 2 K/min. Reaction conditions: $P_{CO} = 0.5 \times 10^{-1}$ mbar, $P_{O2} = 0.5 \times 10^{-1}$ mbar. The Ru(II)-O_{sub} and Ru(I)-$2O_{ad}O_{sub}$ components are labelled as 'ad' and 'sub' in the Ru $3d_{5/2}$, respectively. The component labelled 'Ru_xO_y' correspond to amorphous film which is precursor to growth of the RuO_2 islands, characterised by the component 'ox'[1]. The component used as the zero-energy reference corresponds to metallic bulk Ru at binding energy at 280.1 eV. In the O 1s panel the component at 530.0 corresponds to adsorbed and 'surface oxide' phase, whereas the one at 529.5 eV to oxygen in the RuO_2[1,3]. The position of the O1s component corresponding to CO is indicated as well. It is observed only at temperatures below the real onset of CO_2 production.

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