Oxygen dissolution: *in situ XPS investigation of Pd(111) oxidation*

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1. Introduction

Palladium is considered as the best catalyst for the catalytic combustion of methane, which is an environmentally benign process for power generation with low NOx emissions and to remove residual methane from the emission gases of methane-powered vehicles [1].Catalytic combustion is carried out in stages varying from low temperature, where PdO is the thermodynamically stable phase, to high temperature, where Pd metal is the stable phase. Therefore, the oxidation of metallic Pd is critical for the understanding of catalytic combustion. One important phenomenon is the hysteresis in the oxidation/decomposition cycle; the sample reoxidizes only at a much lower temperature than the one predicted by thermodynamics. Salomonsson *et al.* [2] explained the hysteresis in term of a three-phase system: gas phase O_2, oxygen dissolved the palladium bulk and PdO_x. However, no experimental evidences were proposed.

There are number of 'surface science' studies of oxygen/palladium system [3-8]. The question is can the surface species characterised in great detail under high-vacuum conditions adequately
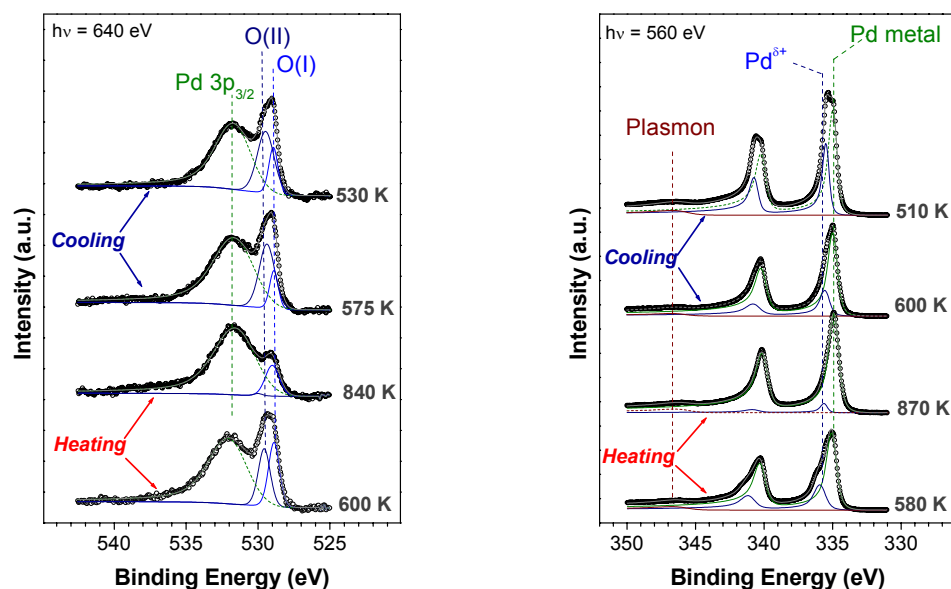

Figure 1 O 1s and Pd 3d spectra obtained *in-situ* during heating and then cooling Pd(111) in 10^{-4} Torr O_2.

represent the dynamic surface chemistry at realistic pressure? In order to address this

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question, the present project aims to investigate the interaction between oxygen and palladium in the mbar pressure range by *in-situ* X-ray photoelectron spectroscopy. The key feature is to correlate adsorbed species formed in the close-to-real-pressure conditions and in UHV.

2. Results

Figure 1 shows O 1s and Pd 3d spectra obtained *in-situ* during heating and cooling cycle of Pd(111) in 10^{-4} Torr O_2. The O 1s spectra were fitted with three components: Pd $3d_{3/2}$ peak (531.9 eV) and two, O(I) and O(II), peaks (528.9 and 529.5 eV) assuming Doniach Sunjic profiles. The O(I) and O(II) peaks, which were observed at 600 K, can be assigned to a 2D surface oxide [4]. The formation of the 2D oxide was supported by high binding energy component in Pd 3d spectra. The $Pd^{\sigma+}$ component disappeared and the O(I) and O(II) peaks lost the intensity after 720 K that evidenced the surface oxide decomposition. Noteworthy, the O(I) component did not disappeared even at 870 K. The nature of the oxygen species was investigated at 600 K and 840 K using depth profiling by varying the energy of incident photon (spectra not shown here). The O(II) component demonstrated the surface nature as was expected for the surface oxide oxygen, whereas the O(I) peak has a surface and bulk contributions. Likely, the O(I) peak represented two oxygen species: oxygen belonged to the surface oxide and oxygen species dissolved in the palladium bulk. Indeed the binding energy of 529.2 V reported for the dissolved oxygen [3] is close to the value of the O(I) peak. The oxygen species and palladium oxidation state observed during cooling in 10^{-4} Torr O_2 were little different those formed during heating. The O(II) component was dominating in the O 1s spectra and the $Pd^{\sigma+}$ peak became more intensive than during the heating stage.
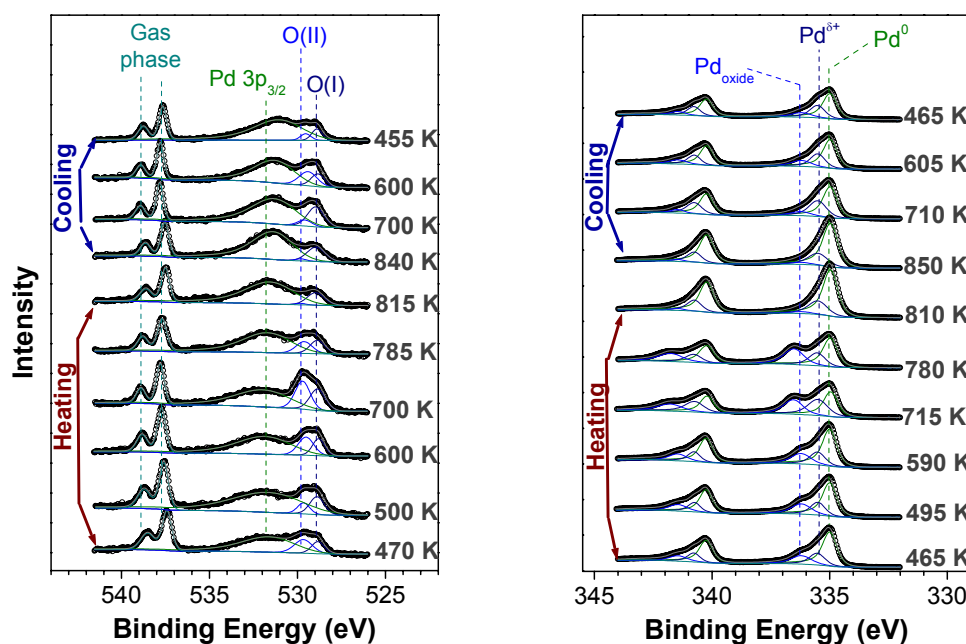

Figure 2 O 1s and Pd 3d spectra obtained *in-situ* during heating and then cooling Pd(111) in 0.5 Torr O_2.

In order to investigate palladium oxidation, the O 1s and Pd 3d spectra were collected when Pd(111) was heating and cooled in 0.5 Torr O_2 (Figure 2). The O 1s spectra contain gas phase contribution as shown in the left panel. As before the O 1s spectra were fitted with three components: Pd $3d_{3/2}$ peak (531.9 eV) and two, O(I) and O(II), peaks (528.9 and 529.5 eV) assuming Doniach Sunjic profiles. The position of the O(I) and O(II) components were not fixed. Pd 3d peaks were fitted with three components, Pd^0, $Pd^{\sigma+}$ and Pd_{oxide}, which were assigned to palladium metal, 2D oxide and bulk oxide. As expected the interaction of oxygen

and palladium proceeded differently in 10^{-4} Torr and 0.5 Torr. The main difference is that the bulk palladium oxide formed in 0.5 Torr O_2 above 600 K: the Pd_{oxide} component (336.6 eV) become well-resolved above 650 K, whereas the O(II) peak shifted towards higher binding energies. This reflected the transformation of the surface oxide to the bulk oxide. The oxidation states of palladium disappeared above 810 K. However, the O(I) peak was observed event at 870 K. This is consistent with the hypothesis about O dissolution. At high temperature, it is easier for oxygen species to overcome the activation barrier and diffuse to the bulk. Thus during cooling, the intensity of O(I) peak increased but oxidation state of palladium did not change noticeably. This mean the oxygen species diffused to the bulk without palladium oxidation. The $Pd^{\sigma+}$ peak started to grow together with the O(II) peak evidencing the 2D oxide formation. However, the O(I) peak was dominated in the spectra. It is very remarkable that no bulk oxide form during the cooling cycle.

3. Summary and Conclusions

The first conclusion is that the 2D surface oxide serves as a precursor of bulk PdO. Indeed the surface oxide can transform to PdO, whereas the bulk oxide did not appear when the Pd(111) surface was cooled in oxygen and the 2D oxide could not form thermodynamically. This is despite the fact that the near surface region was saturated with the dissolved oxygen. This can be explained by high diffusion rate of oxygen to the bulk at high temperature. The adsorption rate is not very high at these conditions and could not provide enough oxygen for oxidation. The surface oxide started to reappear below 600 K but this is to low for oxidation.

The other conclusion is oxygen dissolved in the palladium bulk above 600K. Oxygen dissolution was observed for 10^{-4} Torr and 0.5 Torr treatments. Diffusion of oxygen in the bulk is dominating process at high temperature. Oxygen diffusion occurred oxide precursor. Moreover during cooling it competes with oxidation. The dissolved oxygen led to the surface reconstruction. As shown in Figure 3, the surface structure after 1 Torr oxygen treatment did correspond to a (111) surface. The corrugation was remarkably high that might be due to opening the channel for oxygen diffusion.
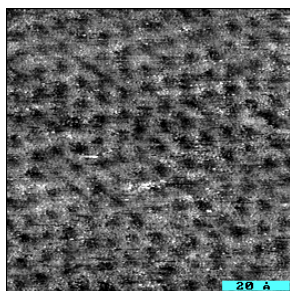
The presented *in-situ* XPS results provided deeper inside of the palladium oxidation. The process started from the surface oxide formation. Likely some imperfections in the 2D oxide acted as a precursor of the bulk PdO. The formation of the surface oxide is not favourable at high temperatures, therefore no the bulk PdO formed during cooling.

Figure 3 *Ex-situ* STM image of the Pd(111) surface exposed to 1 Torr at 820 K for 10 min.

4. Acknowledgement

5. Reference

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