



Kinetics of palladium oxidation and methane oxidation on Pd(111) and (110)

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Palladium is considered as the best catalyst for the catalytic combustion/partial oxidation of methane and other small hydrocarbons, which is an environmentally benign process for power generation with low NO_x emissions and for removal of residual methane from the emission gases of methane-powered vehicles [1]. Investigation of the oxidation mechanism of palladium and the mechanism of oxide decomposition is critical for developing/improving Pd-based catalysts. Palladium oxidation is a complex process consisting of several steps, among them formation of different metastable surface oxide phases [2, 3].

In this project we aimed to study in detailed mechanism of palladium oxidation on Pd(111) and on Pd(110) surfaces, expecting difference in kinetics of the close-packed (111) surface and more open (110) surface.

The kinetics of palladium oxidation was studied by in situ XPS on Pd(111) and Pd(110) surface at 0.2-0.8 mbar O₂ at 275C - 425C. The characteristic O 1s and Pd 3d_{5/2} spectra are shown in Figure 1. Three peak detected in the Pd 3d_{5/2} spectrum are assigned to metallic palladium, Pd(B), to oxidation state, peaks Pd(Ox1) and Pd(Ox2).

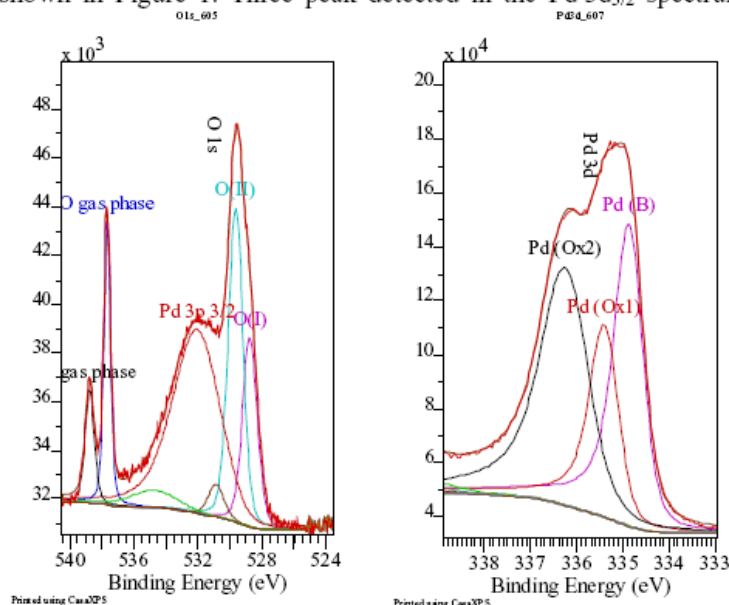


Figure 1. The characteristic O 1s and Pd 3d_{5/2} spectra obtained in-situ during Pd(111) oxidation.

the bulk PdOas shown in Figure 1.

Palladium oxidation can be monitored with the O(II) and Pd(Ox2) peaks as shown for Pd(111) in Figures 2. Palladium oxidation was found to be complex process, which consists of at least 3 stages. The first slow stage is formation of Pd “seeds”. The seed formation is competing with seed decomposition and the resultant rate is depending on oxygen pressure

to oxidation state, peaks Pd(Ox1) and Pd(Ox2). Both the peaks Pd(Ox1) and Pd(Ox2) are characteristics of 2D surface oxide as well as bulk PdO phase. However, when PdO phase appeared the Pd(Ox2) peak dominates as shown in Figure 1. The different phases of the surface oxide demonstrate a different Pd(Ox1)/Pd(Ox2) ratio (see for instance [2, 3]). Oxygen species are characterized by the O(I) and O(II) peaks. The O(II) peak dominate in the case of

and temperature. At high temperature, the seed decomposition is prevailing over seed formation and higher pressure is required to overcome this limitation (the right panel of Figure 2). The second stage is oxide particle growth. A 3D growth of PdO particles was observed during this stage. The PdO particles are supposed to grow from the PdO seeds. The reaction rate at this stage is likely not a function of pressure but temperature. Completed coverage of the surface by the PdO particles results in deceleration of the oxidation process. The third stage is slow oxidation of palladium due to mass-transport limitation. The low reaction rate at this stage is explained by slow diffusion of either oxygen through PdO or palladium atoms towards the surface.

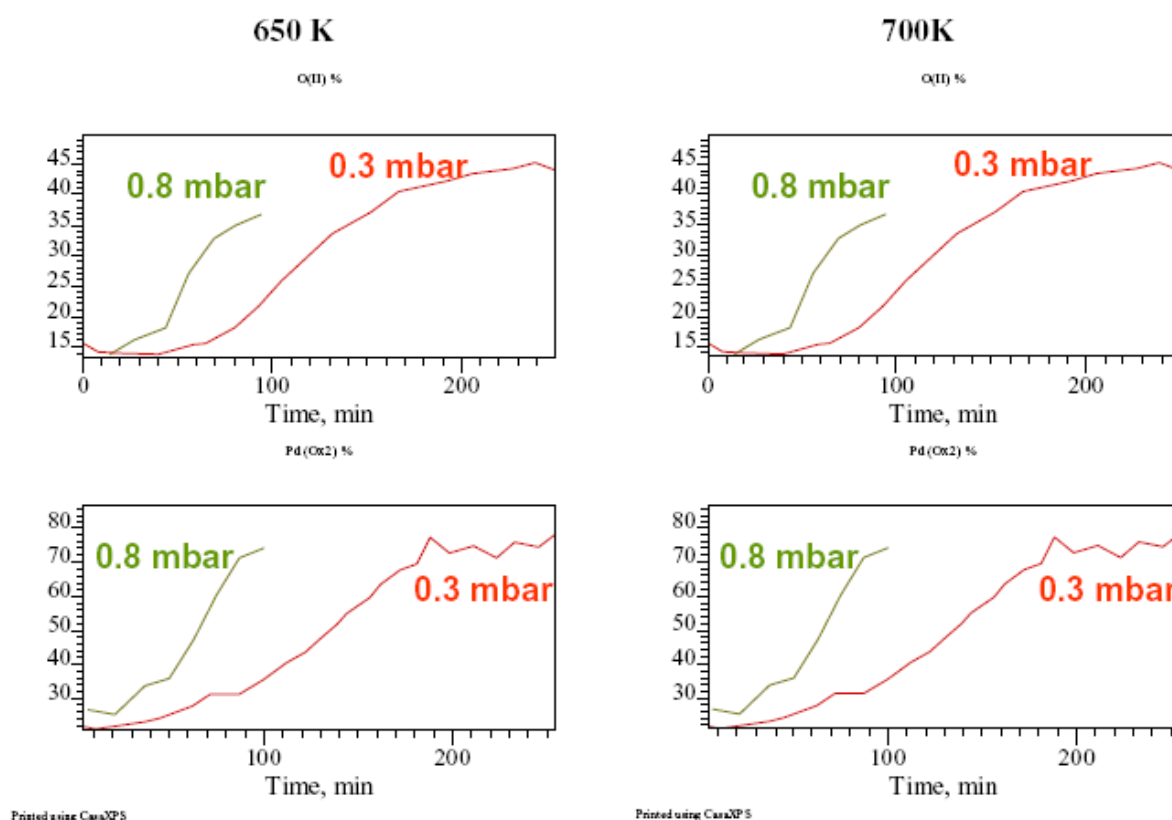


Figure 2. Relative intensity of the O(II) and Pd(Ox2) peaks observed on Pd(111) as a function of the exposure time depending on O₂ pressure and temperature. The left panel: the oxygen treatment was performed at 650K; the right panel: the oxygen treatment was performed at 700K.

Figure 3 represents relative intensity of the O(II) and Pd(Ox2) peaks observed on the Pd(110) surface during oxidation. The open Pd(110) surface oxidises faster and at lower temperature comparing with close-packed Pd(111). The obtained data allow us to draw the full model of palladium oxidation and explain kinetic peculiarities of the process.

The Pd seed are responsible for a catalytic activity maximum of methane combustion on Pd(111) and Pd(110). The activity reaches the maximum at maximum coverage of the PdO seeds. The deeper oxidation did not have such effect as the PdO seed coverage. In general, kinetics of total methane oxidation can be explained in the terms of palladium oxidation.

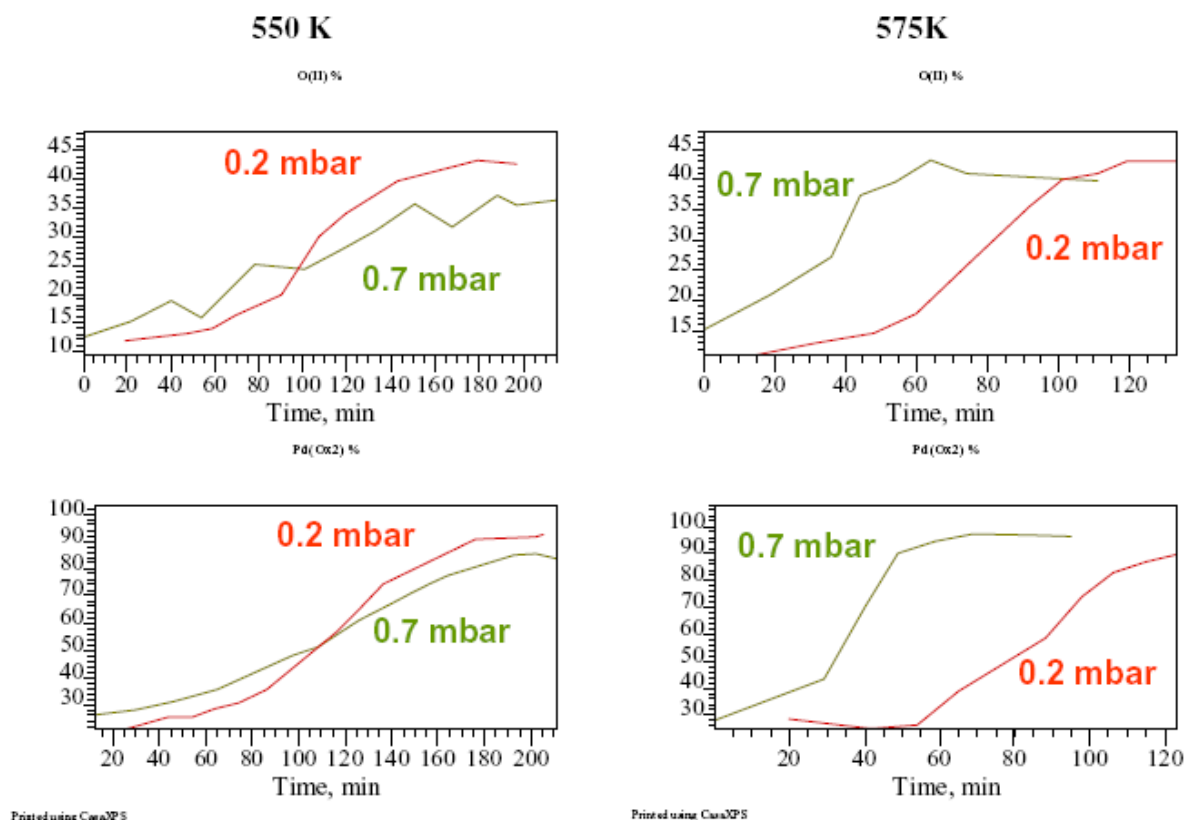


Figure 3. Relative intensity of the O(II) and Pd(Ox2) peaks observed on Pd(110) as a function of the exposure time depending on O₂ pressure and temperature. The left panel: the oxygen treatment was performed at 650K; the right panel: the oxygen treatment was performed at 700K.

References

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