Experiment report CH-4600.

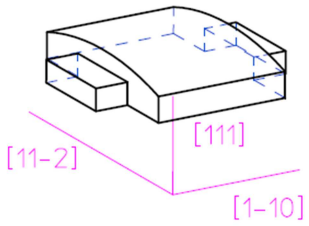
Critical concentration for oxygen-induced step doubling on vicinal (111) Pt surfaces.

1.- Introduction and experimental details

Our previous work on the catalytic activity of Pt997 for CO oxidation near atmospheric pressures [1] clearly evidenced that the vicinal surface carried a structural transformation under specific reaction conditions consisting on a doubling of the terrace and step sizes while maintaining the initial vicinal orientation. Interestingly, the surface having double steps was 2-3 time more active for CO2 production than the single stepped surface. The steps themselves are micro facets of 111 orientation. At variance, the 977 surface which is very similar to the 997 (almost identical terrace size, 111 terraces in both cases) did not show any step doubling under reaction conditions but it has a marked tendency to develop 111 faceting.

To determine if the step doubling in Pt997 was specific to the 997 surface or a general phenomenon, we investigated the microstructures of a curved macroscopic crystal that had in its apex the 111 orientation and away from it (n,n,n-2) vicinals in one side and (n,n-2,n-2) on the other. I. e. the vicinal surfaces, all of them with 111 oriented terraces, had 111 steps on one side of the crystal and 100 on the other.

The crystal , supplied by Bihurcrystal Inc., is depicted schematically in fig 1.



The steps are parallel to the 1-1 0 direction. The crystal was prepared with standard sputter/ anneal procedures and it was mounted in the UHV chamber of EH2 at ID03. The detector was a 2D pixel detector with for modules mounted on the detector arm of the diffractometer

Fig 1. Sketch of the curved crystal.

Many hours were spent to learn how to work with several vicinal surfaces simultaneously. The scan that was considered optimum consisted in setting the appropriate diffraction conditions and scanning the crystal in a direction approximately parallel to the 111 (direction z in diffractometer language). In this way the footprint of the incoming beam swept the crystal surface while impinging several vicinals. Under these conditions, the detector displayed streaks of diffracted intensity which made variable angles with the 111 direction. The streaks of intensity are due to the CTRs tangent to the Ewald sphere at low exit angles. Figure 2 shows some of them.

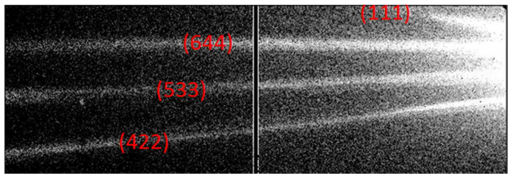
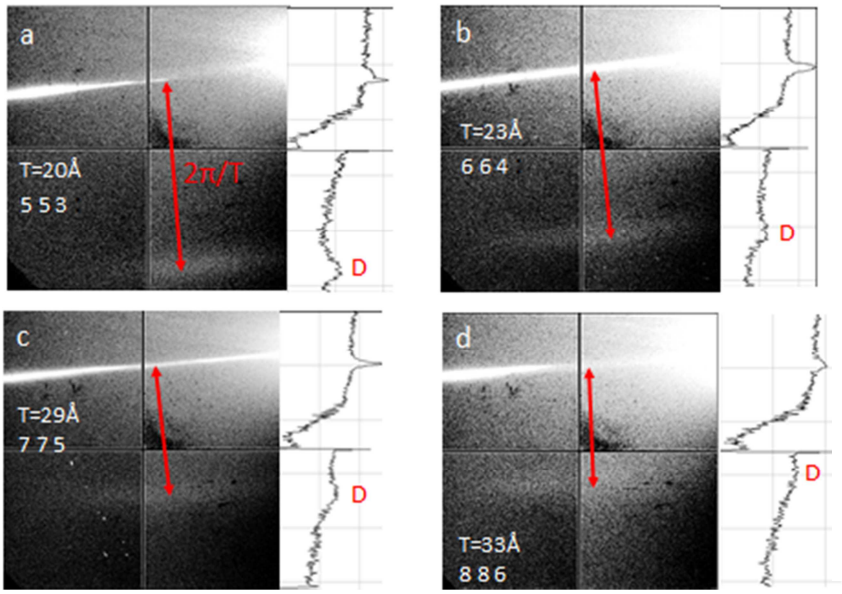


Figure 2. selected CTRs from vicinals to the 111 surface The figure shows some selected CTRs displayed together for illustration. In the experiment, during the z scan, the detector displayed CTR streaks at continuously varying angles.

2.- Results.

The temperature of the clean crystal was set to 150-250 ^{o}C typically and the vacuum system was filled with approximately 4x10 $^{-7}$ mbar of CO and 2x10^{-7} mbar of O_2 by properly adjusting two variable leak valves while keeping the pumping conditions i.e. the gas was continuously flowing. It was impossible to get stable gas flow for more than ~ 20 minutes and it had to be corrected manually. At the same time the gas analyzer was continuously monitoring the CO, O2 and CO_2 in the chamber. Significant CO_2 production was not detected most probably due to the too low pressures of the reactants. However, at temperatures were the reaction is known to occur, a clear structural change was observed in the side of the crystal having 111 steps.

Figure 3 summarizes our observations.



At reaction temperatures, weak and broad intensity streaks parallel to the CTRs appeared in the detector frames. Panels a-d show several of them. The vertical line profiles at the right of the 2D images are from the central part of the images. The broad peaks marked as D are the reaction-induced new diffraction features which correspond to the CTRs of the double step array. The values of T derived from the spacing between the CTR

and the double step CTR depicted in the figure (they are approximate and have uncertainties of around 10%) , indicate the dimensions of the doubled terraces. Consequently, the original vicinals before the doubling had terraces of T/2 dimensions i.e. approximately of 10, 12, 14 and 16 Å for panels a to d respectively and correspond to 553 (terrace 9.6 Å), 664 (terrace 12.0 Å), 775 (terrace 14.4 Å) and 886 (terrace 16.8 Å). These results indicate that the step doubling is not exclusive of the 997 surface as observed in ref. 1 but it seems to be rather general for vicinals with 111 steps. On the other side of the crystal having 100 steps, no terrace doubling was observed.

Reference

1.- O. Balmes et al. ACS Catal. 2016, **6**, 1285