ESRF	**Experiment title:** Modifications of the surface structures of carbon supported Pd nanoparticles by the presence of sulfur adatoms: catalytic consequences	**Experiment number**: CH-4022
Beamline: ID15A	**Date of experiment**: from: 09/04/2014 to: 15/04/2014	**Date of report**: 26/02/2014
Shifts: 18	**Local contact(s)**: Marco Di Michiel	*Received at ESRF:*

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Report:

By using "in situ" high-energy X-ray diffraction technique during the reduction treatment we have observed that initially a palladium hydride is formed and then is transformed into a palladium sulfide (Pd_4S). The catalytic properties of these materials have been tested in the gas phase butadiene partial reduction to butenes. While metallic palladium nanoparticles supported in the same carbon fibers produce butane as principal product, the supported Pd_4S nanocrystals mainly yield different isomers of butenes independently of the conversion level. Furthermore applying the same X-ray diffraction method is revealed that this catalytic phase is stable during reaction.

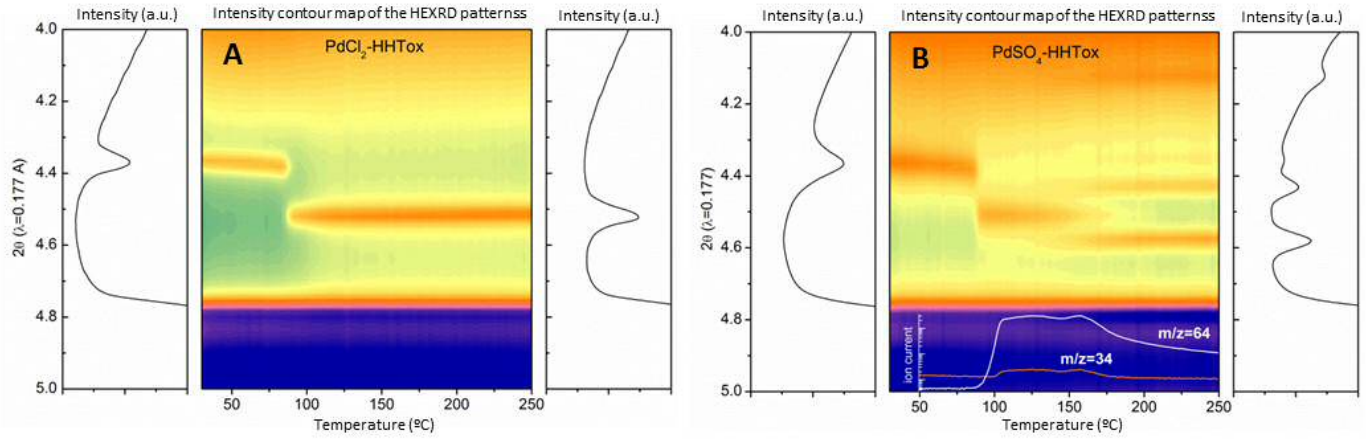

Figure 1. Intensity contour map of the HEXRD patternss obtained during temperature programmed reduction in H_2-He from RT up to 250ºC. A) $PdCl_2$/C B) $PdSO_4$/C. Initial and final HEXRD patterns are showed on the left and right panels, respectively. MS analysis of gases evolved during the heating treatment.is showed in the blue graph insets.

Based on our observations by combining HEXRD and MS measurements we propose that the reduction under hydrogen of the carbon supported palladium sulphate precursor, $PdSO_4$-HHTox sample, provides the Pd_4S based catalyst with superior selectivity to partial hydrogenation of dialkenes.This approach supposes an easy and confident method to synthesize a well-defined single palladium sulfide structure.

Contrarily to Pd metal, where thermodynamically non-stable surfaces and morphologies are required to obtain the desired selectivity, here we present a Pd_4S phase with significant activity, appropriate selectivity and high stability under reaction conditions.

Moreover, an effect of particle size of the Pd_4S phase on the selectivity to partial hydrogenation has been also observed;, crystallites above 11 nm are likely needed for a full selectivity to partial hydrogenation of butadiene.

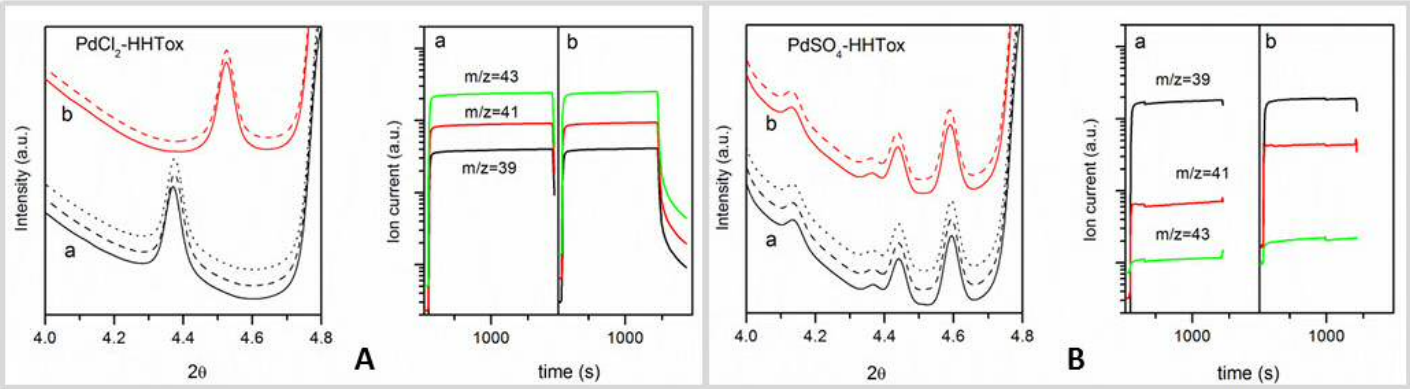

Figure 2. HEXRD patterns obtained under consecutive H_2 (—), H_2+Bd (- - -), H_2 (...) atmospheres at several constant temperatures. (A): $PdCl_2$-HHT_{ox}; a: RT, b: 150ºC. (B): $PdSO_4$-HHT_{ox}; a: 100ºC, b: 160ºC.

Finally, we would lie to thank Dr M. Di Michiel for the extensive support he has given this experiment. Without his support and know-how it could not have been the success that it has turned out to be.