ESRF	**Experiment title:** In situ combined XAFS, SAXS and XRD investigation of the nucleation and growth of Pt and Pt-Me (Me=Co, Ni) nanoparticles for fuel cells application	**Experiment number**: CH-3813
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Report:

Platinum-based nanocomposites are promising catalysts for low temperature fuel cell. It is well known that most features of the platinum-based catalysts (structure, oxidation state, shape, size) are synthesis-dependent and could vary significantly depending on preparation methods, reaction conditions and component composition as well [1,2]. Application prospects of nanoparticles of precious metal for catalysis are thus determined by understanding of their physicochemical properties and by ability to modify these properties in a controlled manner.

There are several types of platinum based catalysts: pure platinum on different support, ad-atoms [3], core–shell [4,5], random alloy [6], and surface Pt-skin. The one of main requirement to all different nanocatalysts is their small size and, as a consequence, high surface area. One of the ways to employ this requirements the use of high-surface-area carbon black, which can be impregnated with catalyst precursors by mixing them in an aqueous solution [7]. The impregnation step is followed by the reduction step, required to reduce the catalyst precursor to its metallic state. The control of the microstructural characteristics of the catalyst in such an approach is usually carried out by varying the nature of carbon support, temperature, pH and water-organic solvent content [8], which may affect crystal growth, orientation, and grain size. Detailed understanding of the mechanism and kinetics of the precursor reduction and particles' growth during both gas flows and heating is a necessary condition to produce highly efficient catalysts with optimized composition and microstructure.

We have investigated nucleation and growth of Pt/C nanoparticles in the process of thermal decomposition of the precursor in a helium, hydrogen, oxygen, and CO atmospheres during the simultaneous heating. To control the nanoparticle formation process at different synthesis conditions (T, heating time) we used XAFS (EXAFS and XANES) method.

Methods.

For preparation of samples, a carbon black powder (VULCAN XC72, Cabot Corp. 240 m2 /g) was used as a support. Pt(acac)2 (Sigma-Aldrich) was used as a precursor. 25 mg of Pt(acac)2 was dissolved in tetrahydrofuran, after which the 100 mg carbon black powder was added in the resulting solution. Then this solution stirred ultrasonically until complete solvent evaporation. The Pt loading in the investigated samples was 25%. Samples were placed into glass capillaries (Hilgenberg GmbH) having a diameter of 1.0 mm and a wall thickness of 0.01 mm. The pure hydrogen was passed through capillaries while heating (heating rate ~2

C/min) with flow rate 5 mL/min. A heated gas stream was used to heat capillaries. Temperature was controlled by a thermocouple. The synchrotron radiation emitted by the bending magnet (magnetic field strength: 0.4 T) was monochromatized with a double crystal Si(111) monochromator. The platinum L3-edge X-ray absorption spectra (XAS) were recorded in transmission mode. The XAS spectra of Pt foil and Pt(acac)2 pellet were recorded at ambient temperature and pressure as references. The energy scale for the Pt L3-edge (11564 eV) absorption spectra was calibrated to the first maximum of the first derivative spectrum of a metallic Pt foil. The sample was heated from 300K to 600 K in depend on using gas and during the heating process the measurement of the XANES spectra were carried out. When the temperature reached 600K, the sample was cooled down to ambient temperature 300K. To determine local atomic structure of final compound upon reaching room temperature EXAFS spectra were recorded and simulated using the IFEFFIT code. The EXAFS data were collected in equidistant k steps of 0.05 Å−1 up to k = 13 Å−1. Analyses of these data were performed by comparison theoretical and experimental spectra using FEFF-8.2 code [10] at the Debye temperature 300 K. For modelling corresponding models such as bulk Pt, Na2PtC2 and PtO2 from atoms.inp database [11] were used. The Debye-Waller factor and R-factor were 0.006 and 0.008 respectively. Collected spectra were corrected, energy calibrated, pre-edge subtracted and post-edge normalized using Athena package [12] based on the IFEFFIT program [13].

Results and Discussions.

At a first step, the kinetics of platinum nanoparticles formation has been studied in a helium atmosphere. A helium-gas flow rate was 5 ml/min. To determine local atomic structure in initial point of the heating we have recorded the EXAFS spectra at room temperature. Then, sample was heated and during the heating process the measurement of the XANES spectra were carried out. The heating was finished when formation of Pt/C nanoparticles was observed and the temperature of the formation was determined. These phenomena could be identified when changes in the shape of XANES spectra were finalized.

After heating, the sample was cooled down to room temperature (25°C). To determine the local atomic structure of nanoparticles upon reaching room temperature were recorded EXAFS spectra. To study nucleation and growth of Pt/C nanoparticles in hydrogen and CO atmosphere we have used the similar procedure.

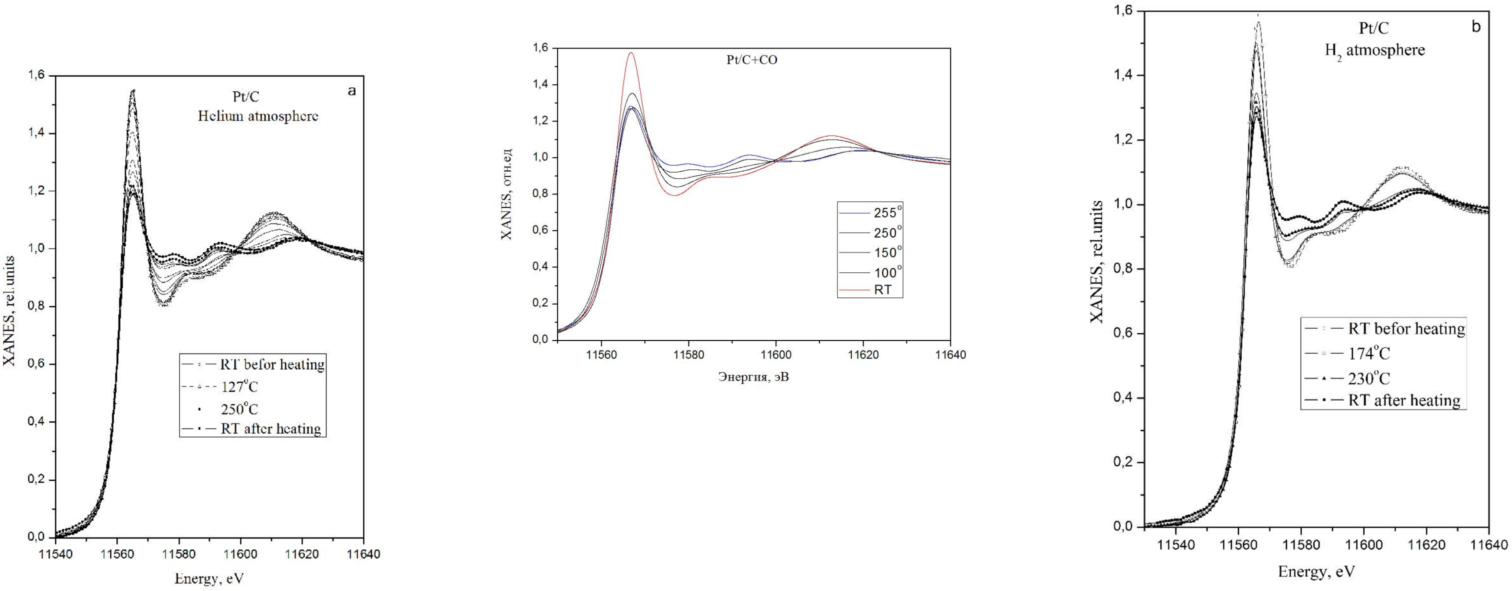

Fig. 1. Normalized XANES spectra of Pt L3-edge in the process of platinum nanoparticles nucleation in a helium atmosphere (a) and hydrogen atmosphere (b) and CO (isert) atmosphere.

Figure 1 shows XANES spectra of the Pt L3-edge in the process of platinum nanoparticles nucleation in a helium (a), hydrogen (b) and CO atmospheres. As one can see, while temperature increases the shape of the absorption spectra changes. At room temperature, the shape of the spectra of the both samples corresponding to the spectrum of Pt(acac)2. As seen in Figure 1 (a), in helium atmosphere precursor decomposition begins at about 120°C that reflected in slight XANES spectrum changes. The shape of spectrum at about 240°C is close to the spectrum of Pt nanoparticles. A further increase in temperature did not lead to a change in shape of the spectra. As seen in Figure 1(b) in hydrogen atmosphere precursor decomposition begins at higher temperatures of about 170°C and the final formation of nanoparticles completes at temperatures of about 250°C. Moreover, for both atmospheres the XANES spectra exhibits a significant decrease in the intensity of the main peak with increasing temperature. The spectrum of the sample before heating shows high white line intensity, indicating a high valence state of Pt. The white line intensity slightly decreases after start of heating process. Changes in the white line intensity during heating are related to the structural changes of the platinum.

We simulated EXAFS spectra using code IFEFFIT to determine the neighborhood of the absorbing atom and to clarify Pt-C interaction. Figure 2 shows the change of Fourier transform of EXAFS spectra observed for catalysts before heating (a) and after heating in helium (b) and hydrogen (c) atmospheres. In accordance to our data before reduction there are two peaks which correspond to Pt-O and Pt-C bond for Pt(acac)2 (at R = 1.95 Å and R = 2.0 Å, respectively). We obtained distances Pt-O, that are in a good agreement with the distances obtained in the works [14] and [15]. Coordination number for Pt-O is N = 4. Figure 2 (b) represents clear peaks, which correspond to Pt-Pt at R = 2.73 Å and Pt-C at R = 2.07 Å with coordination numbers 6 and 0.8, respectively. The presence of these two peaks confirms formation of Pt nanoparticles on carbon support surface. Figure 2 (c) shows the simulation results for Pt(acac)2 on the carbon support in hydrogen atmosphere after process of heating. There are two obvious peaks corresponding to Pt-C at R = 2.03 Å and Pt-Pt at R = 2.75 Å with coordination numbers 0.9 and 6, respectively. Obviously, after heating, the platinum particles formed on the carbon support. We obtained good simulation results; in all cases, R-factor was lesser than 4 % (0.036, 0.024 and 0.008).

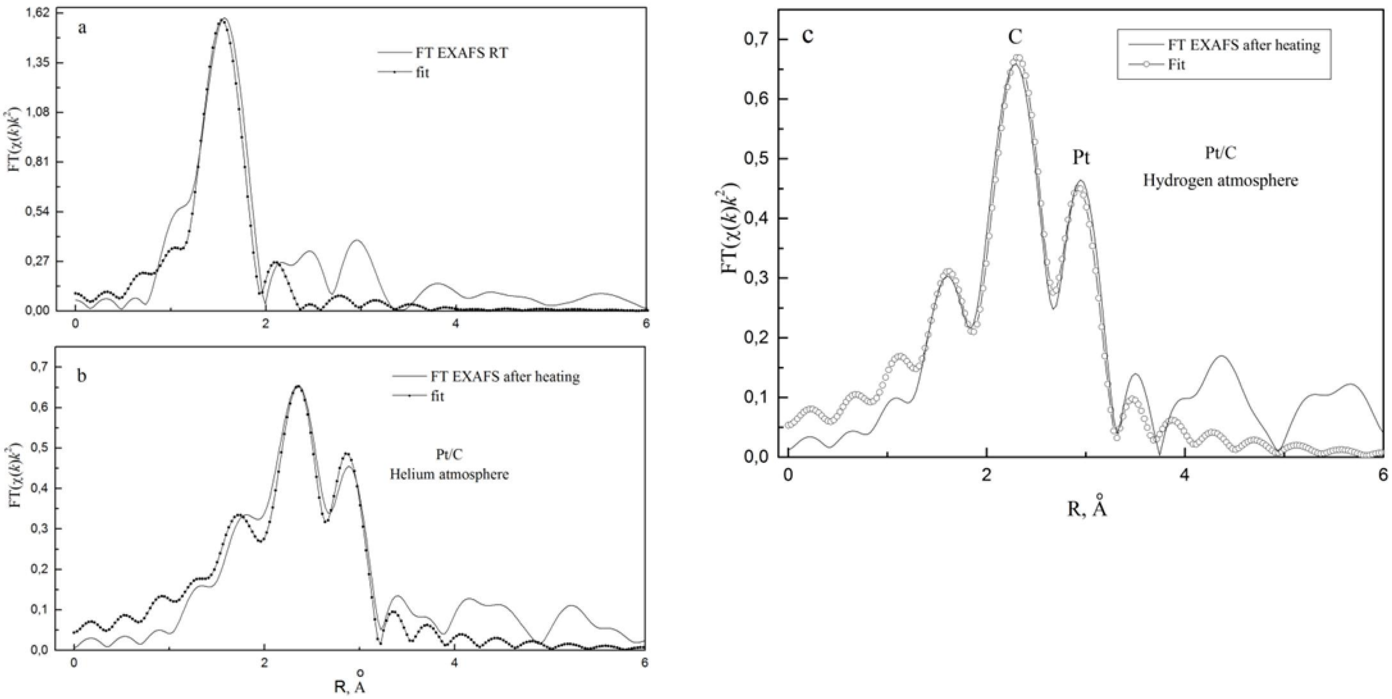

Figure 2. Modeling the Fourier transforms of Pt L3-edge EXAFS spectra for Pt catalysts supported on Vulcan XC-72 before heating (a) and after heating in helium (b) and hydrogen (c) atmospheres.

Conclusion.

Analysis of x-ray absorption spectra XANES for $L_{2,3}$ - platinum registered during the thermal decomposition of the precursor Pt (acac) 2 in the atmosphere of helium, hydrogen and CO showed:

1. No decomposition processes and nucleation Pt/C nanoparticle to a temperature of 130°C under atmospheric types;
2. In a helium atmosphere, the decomposition of the precursor Pt(acac)$_2$ begins at about 120°C. Formation of nanoparticles completes at temperatures of about 240°C.

3. In a hydrogen atmosphere, the decomposition of the precursor Pt(acac)2 begins at about 170°C. Formation of nanoparticles completes at temperatures of about 250°C.
4. In an atmosphere of CO decomposition processes precursor Pt (acac) 2 starting at ~ 170oC. Completion of the formation of Pt / C nanoparticles were observed at ~ 255 ºC.
4. Distances Pt-Pt for the nanoparticles formed in helium atmosphere is shorter in comparison with the nanoparticles formed in hydrogen atmosphere (2.73 Å and 2.75 Å, respectively).

References.

[1] Rodriguez, J.A. Surf. Sci. Rep. 1996, vol. 24. 223 – 287.

[2] Suib, Steven L. New and Future Developments in Catalysis: Batteries, Hydrogen Storage and Fuel Cells. 2013, 217 – 231.

[3] Watanabe, M.; Motoo, J.S. Electroanal. Chem. 1975, vol. 60, 267 – 273.

[4] Mani, P.; Srivastava, R.; Strasser, P. J. Phys. Chem. C. 2008, vol. 112, 2770–2778.

[5] Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Ziu, L.; Kaya, S.; Nord-lund, D.; Ogasawara, H.; Toney, M.F.; Nilsson, A. Nat. Chem. Published Online 25 April, 2010.

[6] Duong, H.T.; Rigsby, M.A.; Zhou, W.-P.; Wieckowski, A. J. Phys. Chem. C. 2007, vol. 111, 13460–13465.

[7] Zhang, J. PEM Fuel Cell Electrocatalysts and Catalyst Layers. Springer-Verlag, London Limited, 2008.

[8] Leontyev, I. Journal of Alloys and Compounds. 2010, vol. 500, 241-246.

[9] Nikitenko S, Beale A, van der Eerden A, Jacques S, Leynaud O, O'Brien M, Detollenaere D, Kaptein R, Weckhuysen B, Bras W 2008 J. Synchrotron Rad. 15 632–640

[10] Ankudinov A, Bouldin C, Rehr J, Sims J, Hung H 2002 Phys. Rev. B 65 104107–104118

[11] http://cars9.uchicago.edu/~newville/adb/search.html

[12] Ravel B, Newville M 2005 J. Synchrotron Radiat. 12 537–541

[13] Newville M 2001 J.Synchrotron Radiat. 8 322–324

[14] Onuma, S.; Horioka, K.; Inoue H.; Shibata, S. Bull. Chem. Soc. Jpn. 1980, vol. 53, 2679.

[15] Beck, I.E.; Kriventsov, V.V.; Ivanov, D.P.; Zaikovsky, V.I.; Bukhtiyarov V.I. Nuclear Instruments and Methods in Physics Research A. 2009, vol. 603, 108–110.