



	<b>Experiment title:</b> <i>Combined in situ XAS and XRD study of carbon-supported core-shell electrocatalysts for oxidation of small organic molecules</i>	<b>Experiment number:</b> 01-01-796
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## Report:

Fuel cells have been attracting much attention as a next generation power source for various applications [1]. Direct methanol fuel cells (DMFC) have 10 times larger volumetric energy density than lithium-ion batteries. Platinum has intrinsically good properties as a component of fuel cells catalysts and therefore is often used on anodes of DMFCs.

Properties of bimetallic catalysts can be significantly influenced by the degree of alloying between constituent elements. Particularly, the surface composition always plays a crucial role in determining the catalytic properties.

Bimetallic core-shell Pt@Ru(1:1)/C, Pt@Ru(2:1)/C and Ru@Pt/C nanoparticles are synthesized in our laboratory at NTNU. Their size is approximately 5nm, they contain 10-20% metal of total catalyst weight and have high tolerance to CO. Their structure was compared with conventional monometallic and bimetallic-alloyed nanoparticles of similar size and composition under reduction conditions.

The structure and reactivity of the nanoparticles were studied *in situ* using XRD ( $\lambda=0.5\text{\AA}$ ) and XAS at Pt L<sub>3</sub> edge and Ru K-edge. Powders were placed in quartz capillaries and heated at temperatures up to 200 °C in reducing atmospheres (5% H<sub>2</sub> in argon) or pure argon.

These nanosized powders were also investigated in a specially developed electrochemical cell during *in situ* electrochemical CO stripping (Fig1). The powders were sprayed onto carbon foil surface using Nafion solution as a binder. The foil was connected to Gamry PCI4 potentiostat as a working electrode. Palladium mesh served as a counter electrode. A dynamic hydrogen electrode in a Luggin capillary was used as a reference.

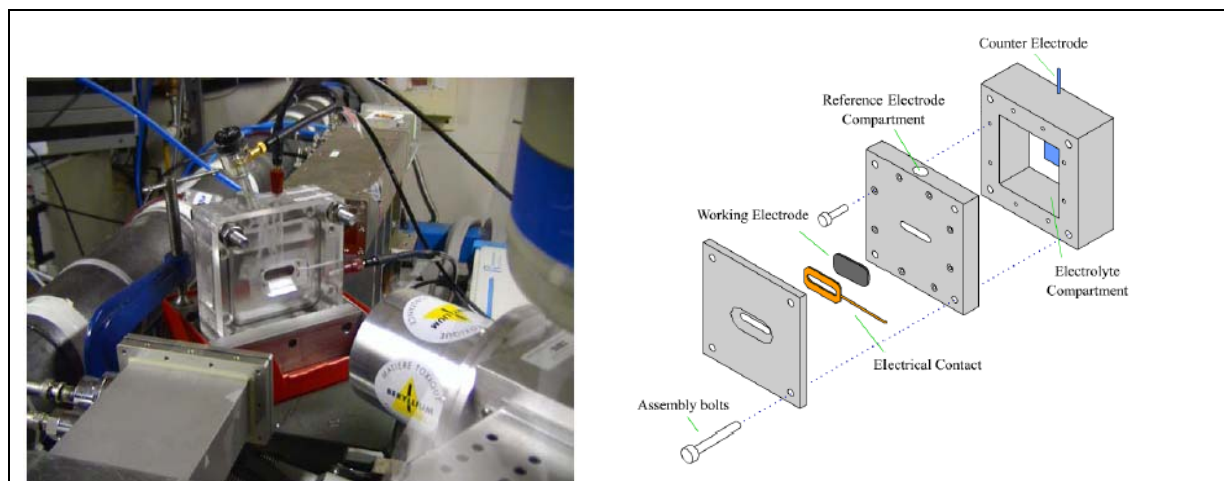


Figure 1. Photo and scheme of the in situ spectra-electrochemical cell

Combined XRD and EXAFS study of Pt(core) @Ru(shell) samples with different thicknesses of Ru shell confirmed that Pt cores with size distribution centered around 3 nm and corresponding coordination numbers of 9-10 were formed. The Ru shell is too thin to give any XRD signal, and that correlates with EXAFS results giving very low coordination numbers. Ru coordination numbers increase with an increase of the shell thickness, but the values are low, indicating very amorphous state of Ru in the particles. That correlates with results of electrochemical tests. Very low values of Pt-Ru coordination number confirm formation of the core-shell structure.

Another very important result was obtained in the experiment when core-shell and Pt-Ru/C alloy samples were heated in hydrogen-contained atmosphere. In case of alloy the particles demonstrated a tendency to grow, which is in a good agreement with the literature due to very high mobility of Pt in the presence of hydrogen (Figure 2). No changes in Pt particle size were detected for the core-shell system, therefore the formation of the true core-shell particles was confirmed.

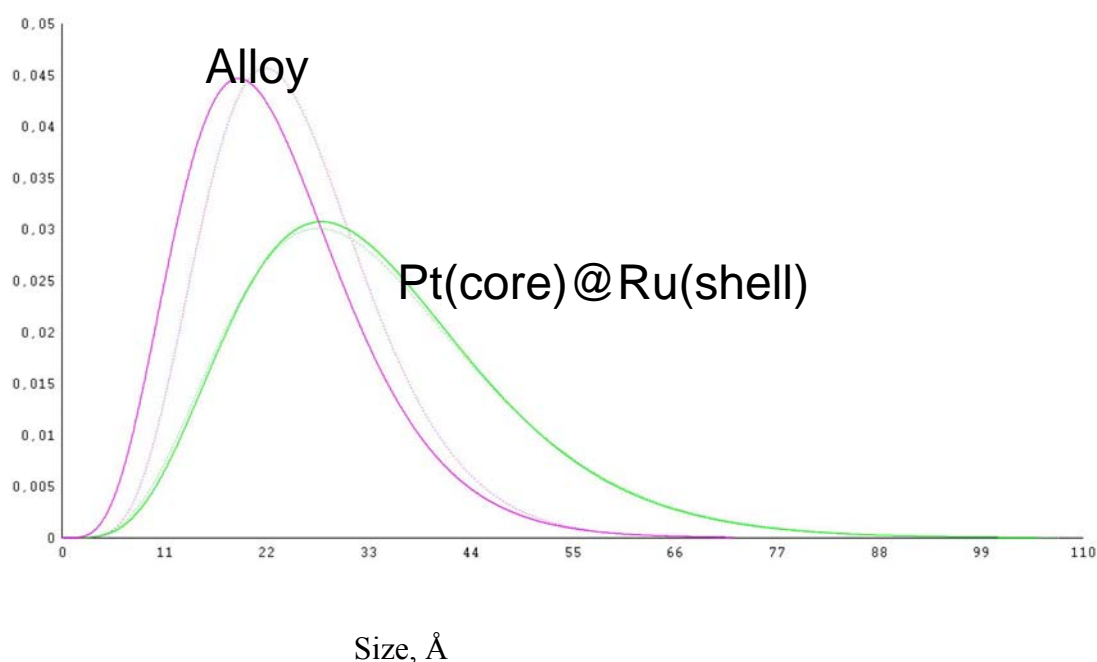


Figure 2. Crystallite size distribution for Pt-Ru/C and Pt(core)@Ru(shell)/C heat-treated in argon (dark curves) and 5% hydrogen in argon (light color).

The Ru(core)@Pt (shell) system was also investigated. It seems that the Ru core is amorphous and consists of small agglomerates. No crystallization of the core was detected at the experimental conditions. Hence, it is interesting to follow Ru crystallization at higher temperature in such small core-shell particles and reveal the mechanism of the crystallization, as well as possible mechanism of surface segregation.

The data obtained during oxidation of CO and methanol in the in situ cell is still under analysis.