

**Experiment title:**

The sulfur tolerance of supported platinum catalysts

**Experiment number:**

CH95

**Beamline:**BM29  
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1996**Shifts:****Local contact(s):**

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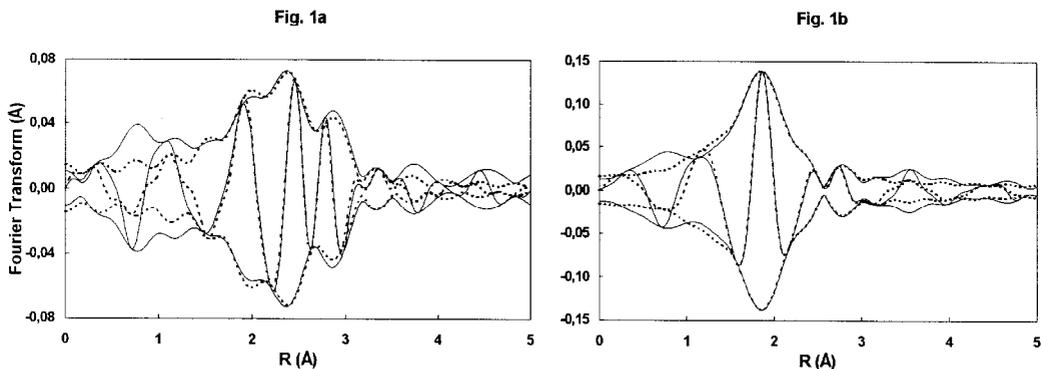
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**Report:**

**Introduction.** Supported noble metal catalysts are susceptible to poisoning by sulfur. Conventional Pt/alumina reforming catalysts operate quite well feed sulfur levels up to 1 ppm. Paraffin isomerization catalysts (Pt/acidic zeolite) operate well with even higher feed sulfur levels. Newly developed PdPt/Zeolite catalysts for deep aromatics saturation of automotive gasoil show a sulfur tolerance upto 1000 ppm [1]. For hydrodearomatization and desulfurization of gasoils, for example noble metal catalysts must be developed which can tolerate even higher sulfur levels. Despite the numerous studies of sulfur poisoning and its tremendous economic consequences, a clear understanding of the effects of sulfur on supported metal catalysts and the roles of various catalyst properties both of the metal and the support in improving sulfur tolerance is still lacking. XAFS experiments on reduced and sulfur poisoned platinum particles supported on a high surface area saponite (synthetic clay mineral) are described below.

**Figure 1 :** R - space fit: FT,  $k^1$ ,  $3.5 < k < 12.0 \text{ \AA}^{-1}$ ,  $1.7 < R < 3$ .  
 1a: Pt-saponite after reduction  
 1b: Pt-saponite after reduction treated with hydrosulfide



**Results.** Figure 1a (solid line) gives the Fourier transform of the EXAFS data of a Pt/Saponite catalyst after reduction in flowing hydrogen at 300°C. Fitting in r-space (dotted line) shows that the platinum particles are fully reduced with an average co-ordination number of 5.2 (particle size about 12 Å) and a Pt-Pt distance of 2.76 Å. An interfacial Pt-O co-ordination could be analysed with a distance of 2.55 Å, characteristic for the structure of the interface between very small platinum particles and oxide supports measured in the presence of hydrogen. Treatment with a mixture of H<sub>2</sub>S/H<sub>2</sub> at 250°C leads to a disruption of the platinum particles. The change in structure after H<sub>2</sub>S/H<sub>2</sub> treatment as can be seen by comparing the Fourier transform of the sulfur poisoned catalysts (Figure 1b) with the corresponding Fourier Transform of the freshly reduced catalysts (Figure 1a). Fitting in r-space resulted in a Pt-Pt co-ordination number of 2.7 (particle consisting of 3-4 atoms) with a significant smaller Pt-Pt distance of 2.69 Å. In addition Pt-S bonds with a distance of 2.28 Å were analysed. Also the structure of the metal-support interface is altered after sulfur chemisorption, a much shorter Pt-O distance of 2.2 Å is detected. The disruption of the platinum particles together with a change in the metal-support interaction after sulfur chemisorption is a unique observation, which can only be obtained with in-situ XAFS spectroscopy.