	<b>Experiment title:</b>  Electron density changes in carbon-carbon composite supported Au catalyst heated by the Joule effect	<b>Experiment number:</b>  CH2381
	<b>Beamline:</b>  BM01B	<b>Date of experiment:</b>  from: 05.04.07 to: 10.04.07
<b>Shifts:</b>  15	<b>Local contact(s):</b>  Wouter van Beek	<i>Received at ESRF:</i>
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## Report:

The study of catalysis by gold has attracted increasing interest since the demonstration of low-temperature CO oxidation on metal oxide supported gold nanoparticles [1]. Despite the attention, the reaction mechanism and the nature of the active sites remains a subject of debate. The activity of supported gold catalysts has been found to be dependent on preparation method, Au particle size and Au-support interactions. Deposition of highly dispersed Au particles in the presence of carbon is not a trivial task due to the tendency towards agglomeration of the Au. In addition, the catalytic stability and activity are controlled by the state and morphology of the support material. The selection of an efficient support is thus a decisive factor to provide the desired contact between the Au particles and the substrate [2].

Nanoparticles of  $\text{TiO}_2$  is used for many applications due to modified electronic and optical properties. The two common phase of the oxide is anatase and the thermodynamically more stable rutile. However, anatase phase can not only transform to the rutile phase, but also easily agglomerate at elevated temperatures. Hence, special care must be taken to control the crystallinity, phase composition and morphology features of

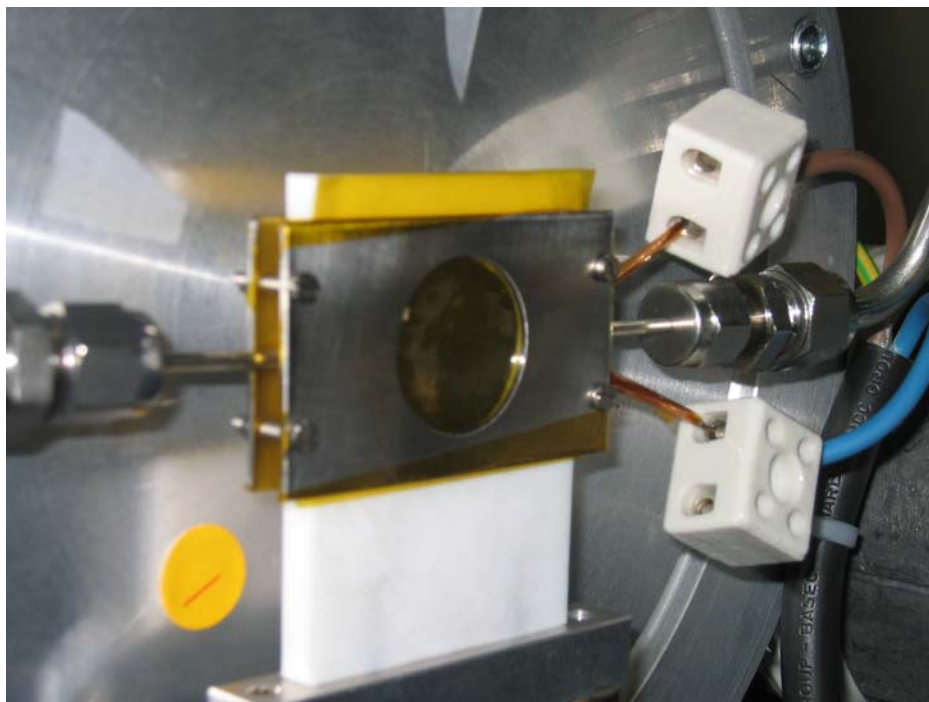
titania to obtain desired properties of the oxide. Fraction of the rutile in the anatase phase can enhance the properties due to the electron and hole transfer between the two phases.

Graphitic carbon materials such as carbon felt (CF) and carbon nanofibres (CNF) have relatively high thermal conductivity. It is therefore possible to utilise the material as an electronic conductor between two electrodes. Introduction of a current will provide heating by the Joule effect [3,4].

## Experimental method:

XAFS were collected at the Ti K edge (4966 eV) in transmission mode.

The cell consists of a sample cell with Kapton windows that can withstand temperatures up to 400°C. The cell is heated by the Joule effect. This is possible by utilising the catalytic support material as an electric conductor between two electrodes. The gas flow and the temperature can be controlled and monitored from outside the X-ray hutch. The experiments were performed at atmospheric pressure. The cell set-up is shown in Figure 1. The feed consisted of 5% CO/He and 21% O<sub>2</sub>/He with a total flow of 15 ml/min. The stoichiometric ratio between CO and O<sub>2</sub> was 1:2. Full EXAFS scans were collected at room temperature before exposing the catalysts to the reaction gases. The catalysts were heated to 150 °C and short scans of the edge profiles of the Ti edge were collected during reaction conditions. The samples were cooled to room temperature before scans of the entire EXAFS region were collected.



*Figure 1: Cell set-up for CO oxidation with internal heating by the joule effect.*

## Results:

The pre-edge region of  $\text{TiO}_2$  contains useful structural and electronic information. The pre-edge feature of anatase display four features (A1-A3 and B). The feature A2 can be observed as a weak shoulder on the low energy side of A3 and requires good energy resolution to be observed. Despite the similar crystallographic and electronic structure of anatase and rutile, the A2 peak does not appear to be present in the XANES of the thermodynamically more stable rutile phase. The XANES spectra for the Ti K-edge for some of the samples are given in Fig. 2.

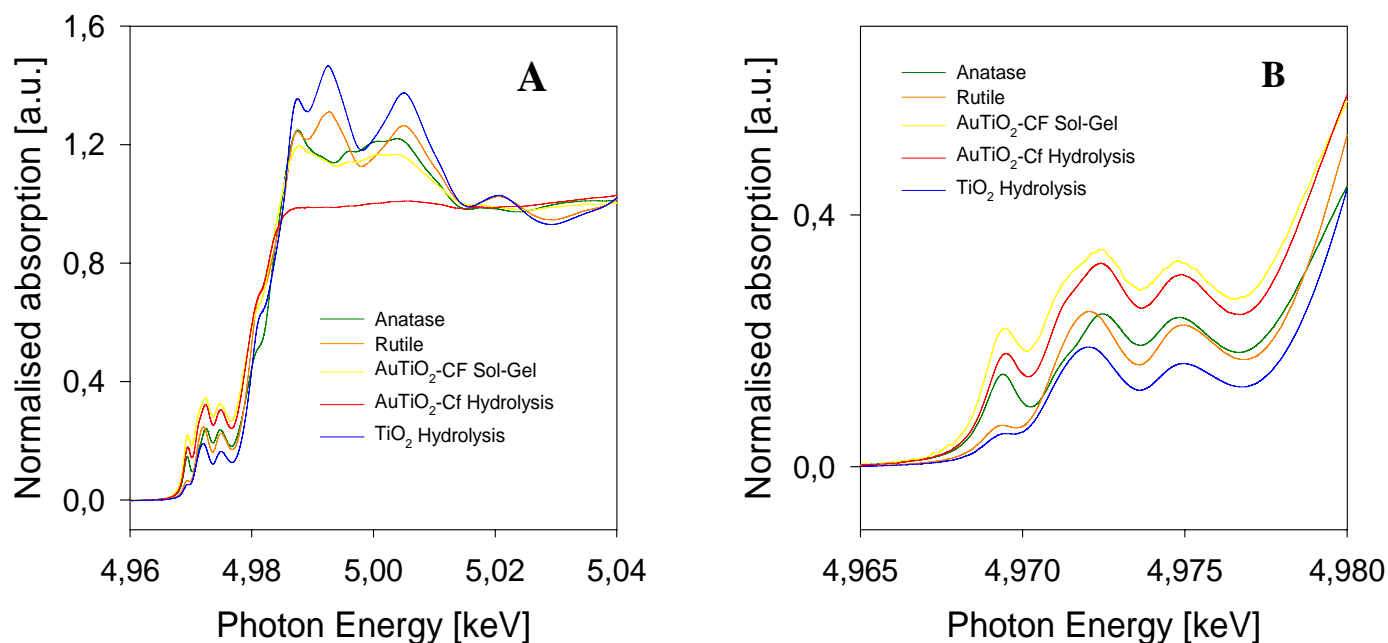


Figure 2: A) XANES spectra of the Ti k-edge and B) magnification of the pre-edge region.

Visual inspection of the pre-edge confirms that the A2 is present in the  $\text{TiO}_2$  supported samples but not in the sample of unsupported  $\text{TiO}_2$ . Differences in intensity of the pre-edge due to particle sizes can be observed and as the particle size decreases the A2 becomes more pronounced. This shows that the  $\text{TiO}_2$  supported on carbon composite contains smaller particles and that the carbon composite is able to stabilise the  $\text{TiO}_2$  during heat treatment. The peaks A1 and B are more intense in  $\text{TiO}_2$  supported on CNFCF. The increase in intensity is induced by an increased distortion of the Ti environment. The distortion of the  $\text{TiO}_2$  structure is a result of the interaction with the CNFCF interface.

Spectra of the Ti k-edge for  $\text{TiO}_2$  prepared by hydrolysis and sol-gel methods are similar in the pre-edge region. However, the post-edge region (4.98-5.02 keV) is quite different, indicating that the  $\text{TiO}_2$  prepared by the sol-gel method is more crystalline than  $\text{TiO}_2$  prepared by hydrolysis.

Also the influence of the structure of the carbon support has been studied. The pre-edge features have similar shape but the intensity of the post-edge is different. The intensity is lowered for the more crystalline

graphite support compared to the platelet and the fishbone structures. A more careful investigation of the EXAFS spectra is necessary to elucidate how the coordination number of Ti influence the spectra.

Further analysis of the XANES profile and EXAFS profile is ongoing.

## References

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