| ![ESRF logo] ESRF | **Experiment title:** Comparison of the Ti K-edge during CO oxidation with use of external and internal heating. | **Experiment number**: 01-01-710 |
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## Report:

Gold has traditionally been known as a catalytic inactive material. However, small supported gold particles exhibits interesting catalytic properties as demonstrated for CO oxidation at low temperatures [1]. The mechanisms leading to catalytic activity are still being debated due to the complexity of particle support interaction and reaction pathways. It has been shown that the activity and particle size depend strongly on the support material, the synthesis method and the activation procedure. It has been reported that the difference in catalytic activity of a Au catalyst on reducible and irreducible support can be explained by a difference in Au particle geometry only, without invoking other support-induced effects [2]. Density functional theory (DFT) calculations and IR measurements indicate that low-coordinated Au atoms are crucial to the catalytic activity of Au catalysts. This parameter seems to be the only that can explain changes in catalytic activity by several orders of magnitude. The gold atoms located at the corners of the Au particles are expected to contribute most to the overall activity. Since the support determines the final Au particle shape through interface energy [3] the selection of an efficient support is thus a decisive factor to provide the desired contact between the Au particles and the substrate. Nevertheless, the reducible supports can be advantageous

because they often contain oxygen vacancies that can serve as Au anchoring sites. Also the number of low-coordinated atoms can be expected to increase with increasing oxygen vacancy density in the support due to more attractive Au-support interactions, which unquestionably affects the catalytic activity of the $Au/TiO_2$ catalyst.

The two common phases of the $TiO_2$ are anatase and the thermodynamically more stable rutile. However, anatase phase can not only transform to the rutile phase, but also easily agglomerate to a bulk form 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.

Graphite 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 [4,5]. However, the use of carbon as a catalytic support for $Au/TiO_2$ requires a different preparation method for obtaining small Au particles compared to Au catalysts supported on pure oxide, which usually is prepared by deposition-precipitation [6]. Also, the preparation of the $TiO_2$ and the following attachment to the carbon material is a challenge. The loading of the $TiO_2$ attached to the carbon, particle size, residue of impurities and the structure varies with use of different preparation methods and will influence the catalytic activity.

## Experimental method:

XAFS were collected at the Ti K edge (4966 eV) in transmission mode. Higher order harmonics were suppressed by tuning the monochromator crystal to 70 % of maximum intensity.

Two different *in situ* cells have been used to elucidate potential changes in the material caused by introduction of a current in the sample. The cells consist of a sample cell with Kapton windows that can withstand temperatures up to 400°C. The two cells are designed for use of different heating methods; 1) heating by the Joule effect utilise the catalytic support material as an electric conductor between two electrodes and 2) use of external heating. The gas flow and the temperature can be controlled and monitored from outside the X-ray hutch. The gas outlet was continuously monitored by a mass spectrometer. The experiments were performed at atmospheric pressure. The cell set-up for heating by the Joule effect is shown in Figure 1. The feed consisted of 5% CO/He and 5% $O_2$/He with a total flow of 15 ml/min. The stoichiometric ratio between CO and $O_2$ was 1:2. Full EXAFS scans were collected at room temperature before exposing the catalysts to the reaction gases. The catalysts were heated to 200°C and short scans of the Ti edge profiles were collected during reaction conditions. The samples were cooled to room temperature before scans of the entire EXAFS region were collected and the cycle was repeated.
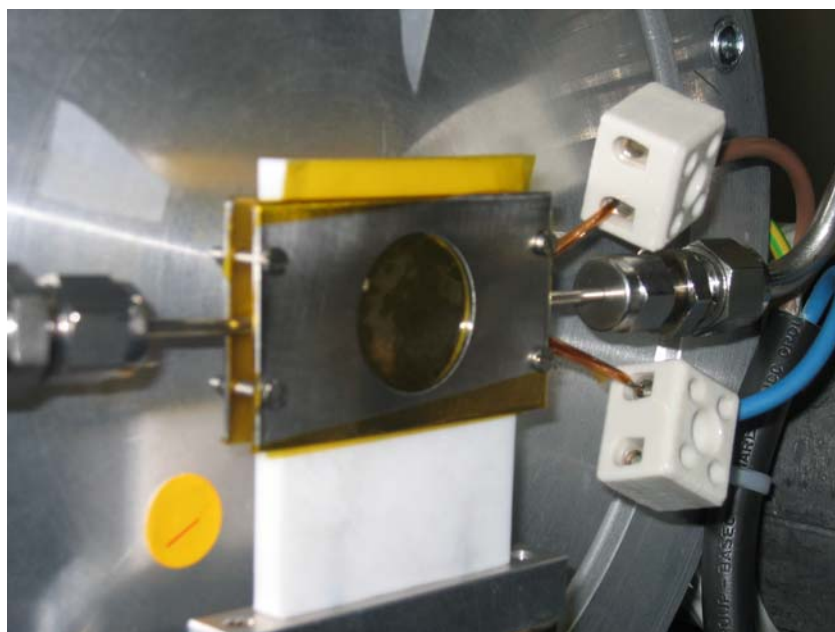
*Figure 1:Cell set-up for CO oxidation with internal heating by the joule effect..*

## Results:

XANES of an X-ray absorption spectrum can be conveniently divided in two regions. The pre-edge region of $TiO_2$ contains much 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 similarity between 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 during CO oxidation are presented in Fig 2.
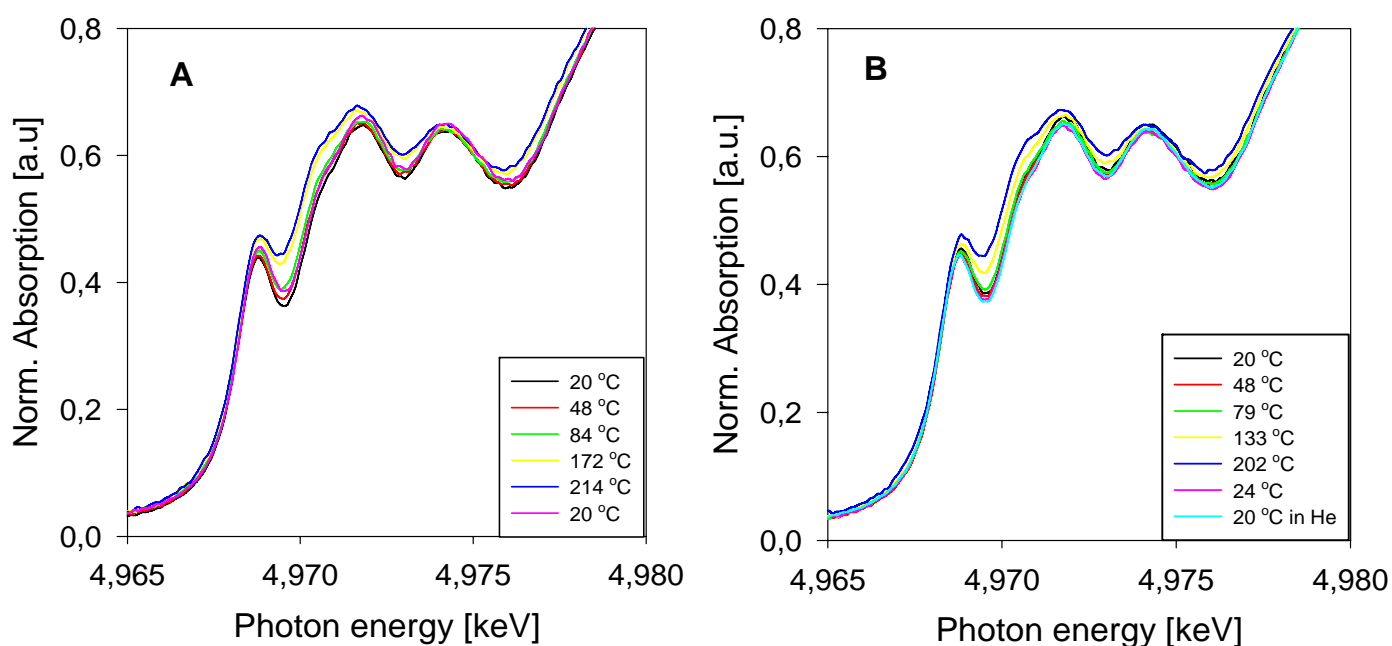


*Figure 2: Comparison of the Ti pre-edge for A) the first cycle and B) the second cycle at different temperatures during CO oxidation with external heating.*

The pre-edge of Ti confirms that TiO$_2$ is present in the anatase phase and that no phase changes occur during the reaction cycles. The intensity of the A1-A3 peaks increases with reaction temperature. However the B peak is unchanged and the changes are reversible. Reversible changes in the pre-edge features can also be observed when the heat is generated by the Joule effect. However, the intensity changes that occur is different. A more pronounced increase in the A2 peak is observed wehereas A1 and A3 are unchanged and B decreases. This indicate that the current in the system influence the structure and could explain the differences in activity behaviour.

The TiO$_2$ supported on carbon exhibit XANES pre-edge peaks with greater intensity than the peaks for anatase. This indicates that Ti no longer resides completely in octahedral sites when it is deposited on carbon. Two different preparation methods have been used for the TiO$_2$. The preliminary results show that the structural parameters obtained from EXAFS and the catalytic activity are markedly different for the two preparation methods. A thorough characterisation is necessary to elucidate the different behaviour in activity and to see how the Au geometry is influenced by the oxide.

Further analyses of the XANES and EXAFS profiles are in progress.

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