



	Experiment title: In situ XAS study on the effect of preparation method on the TiO ₂ structure in Au-TiO ₂ catalyst supported on carbon nanostructures	Experiment number: 01-01-764
Beamline: BM01B	Date of experiment: from: 17.04.08 to: 21.04.08	Date of report: 22.04.2008
Shifts: 15	Local contact(s): Olga Safonova	<i>Received at ESRF:</i>
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Report:

Gold has shown to exhibit high catalytic activity for various reactions such as CO oxidation, water-gas shift reaction and preferential CO oxidation in the presence of hydrogen. The Au particles are most commonly supported on oxide in powder form, such as TiO₂, CeO₂ and Fe₂O₃ [1]. However, powder can be a problem in catalytic reactions due to pressure drop over the catalytic bed. This can be avoided by anchoring the metals on a structured support material.

The use of CNF as support material in heterogeneous catalysis has attracted growing interest due to their specific characteristics. The size and morphology of the CNF provide high surface areas while maintaining macroscopic pore sizes and hence good transport properties in the reactor, and reduced risk of micropore-induced diffusion limitations. The CNF are also resistant to acid/base media and the precious metals can easily be recovered by burning off the support [2]. The CNF can be grown directly onto structured supports such as carbon felt [3,4], foams [5] and monoliths [6] by chemical vapour deposition using nickel as a

catalyst. Gold catalysts on carbon supports are so far most commonly used for liquid reactions, such as oxidation of alcohols and sugar.

The two common phases of the TiO_2 are anatase and the thermodynamically more stable rutile. However, the 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. The fraction of rutile in the oxide can enhance the properties due to the electron and hole transfer between the two phases.

Carbon nanofibres (CNF) have been used in the present work to disperse and stabilise the TiO_2 support and hence the Au particles. Earlier characterisation and activity test of these catalyst systems have shown that the carbon support introduces changes in the active phase compared to catalyst in powder form and also a higher stability in the water-gas shift reaction has been demonstrated.

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.

An in situ cell has been designed to elucidate the feature of TiO_2 during the CO oxidation. The cell is heated by use of Cartridge heaters and consists of a sample cell with Kapton windows that can withstand temperatures up to 400°C. 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 feed consisted of 5% CO/He and 10% O_2 /He with a total flow of 15 ml/min and the gas outlet was monitored continuously by a mass spectrometer. The stoichiometric relationship 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 the temperature was held for 1 hour. 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 and the cycle was repeated. Also, a calcination experiment of the as-prepared $\text{AuTiO}_2\text{CNFCF}$ was performed. The sample was heated to 400 in 5% O_2 /He and the temperature was held for three hours before cooling to room temperature. The XAS data were collected in the same manner as stated previously.

Results:

The pre-edge region of TiO_2 contains useful structural and electronic information. The pre-edge feature of anatase display four features (A1, A2, 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 the

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.

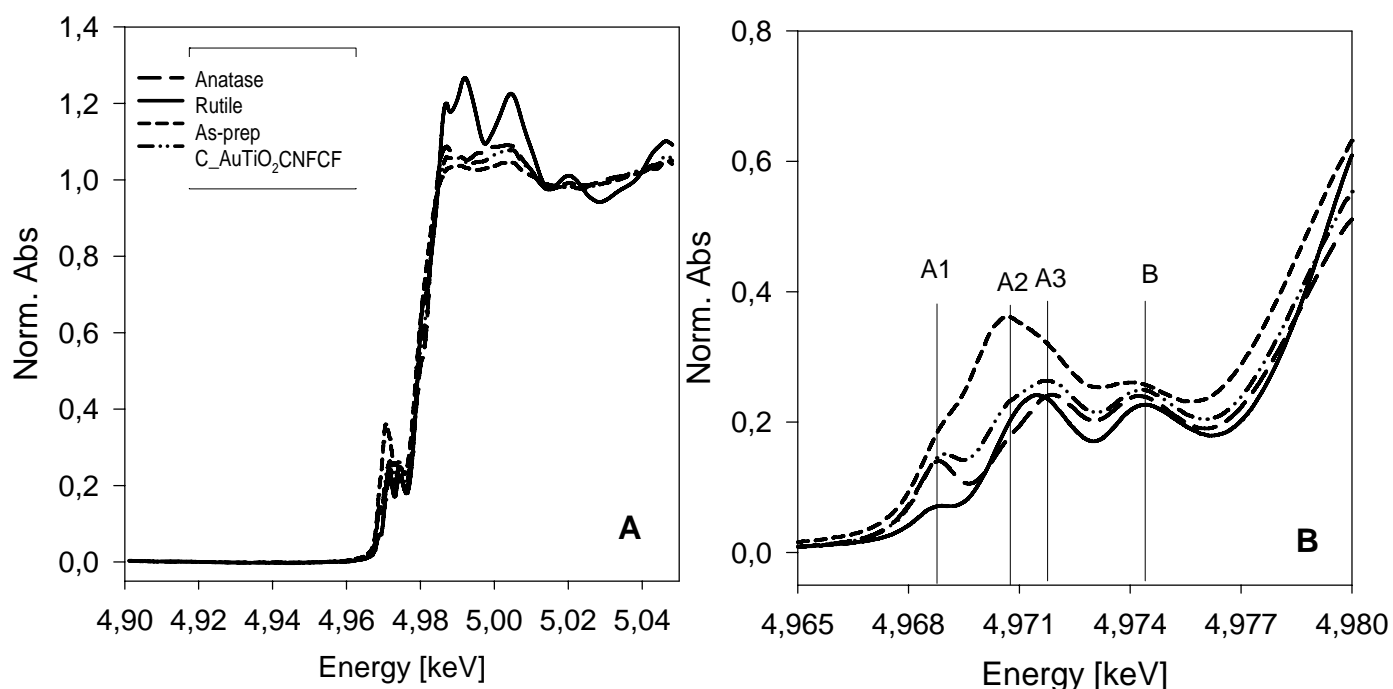


Figure 1: A) The XANES spectra for asprepared $\text{AuTiO}_2\text{CNFCF}$, calcined $\text{AuTiO}_2\text{CNFCF}$, rutile and anatase and B) magnification of the pre-edges. The spectra are recorded in inert atmosphere.

Figure 1A show the XANES spectra of asprepared $\text{AuTiO}_2\text{CNFCF}$ and calcined $\text{AuTiO}_2\text{CNFCF}$ compared to the spectra of the reference models (rutile and anatase). The XANES of the Ti K-edge confirms that the TiO_2 is presented in the anatase phase. No phase changes occurred during the reaction cycles. However, some increase in intensity of the A1-A3 peaks could be observed due to increased temperature. The changes were reversible.

The intensity of the pre-edge transitions are sensitive to the symmetry of the surrounding atoms. Being dipole forbidden, they are weak in symmetrical environments and increase in intensity as the environment is distorted. Figure 1 B) show that the intensity of the pre-edges of asprepared $\text{AuTiO}_2\text{CNFCF}$ and calcined $\text{AuTiO}_2\text{CNFCF}$ are higher compared to commercial anatase. This means that a larger distortion in the environment of TiO_2 occurs when it is deposited onto a carbon support. The as-prepared sample shows a quite different pre-edge compared to the calcined sample. The A2 peak intensity is higher and a energy shift can be observed. Changes in A2 intensity have been correlated to the amount of distortion from perfect octahedral coordination and the energy of this peak has been coorelated with the number of coordinating oxygens. For the as-prepared sample a shift to a lower energy compared to the calcined can be seen due to a lower coordination environment for the central Ti atom. This indicates that the TiO_2 is 5 coordinated before

calcination and increases to 6 coordinated. This will be addressed in the further analysis of the XANES and EXAFS profiles.

References

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