ESRF	**Experiment title:** Local structure of amorphous or partially crystalline TaxOy and NaTaxOy photocatalysts studied by PDF analysis	**Experiment number**: MA-3621
Beamline: ID11	**Date of experiment**: from: 01.11.2017 to: 03.11.2017	**Date of report**: 02.02.2018
Shifts: 6	**Local contact(s)**: Dr. Carlotta GIACOBBE	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Claudia Weidenthaler*

Dr. Harun Tüysüz*

Dr. Wolfgang Schmidt*

Ezgi Onur Sahin*

Simone Gallus*

Dr. Gun-hee Moon*

Max-Planck-Institut für Kohlenforschung, Department of Heterogeneous Catalysis, Kaiser-Wilhelm-Platz 1, 45470, Mülheim an der Ruhr, Germany

Report:

According to the recent research of our group, Ti, Ta and Na/Ta based amorphous photocatalysts yielded better photocatalytic activity compared to the crystalline oxides[1]. The catalysts were synthesized at room temperature via the so-called ´direct injection´ method. The metal ethoxide precursor is injected in a photocatalytic cell containing a water and methanol mixture. The cell is illuminated with UV light. In order to understand the structure-property relationships the local structures of these photocatalysts were analysed using pair distribution function (PDF) analysis[2].

Powder diffraction measurements were carried out at the ID11 beamline using 87.4 keV corresponding to a wavelength of 0.14181 Å. The data were collected between 0.8 – 33 $Å^{-1}$. All samples were sealed in 0.5 mm diameter borosilicate capillaries. An empty capillary was measured as background. PDFs were generated using PDFgetX3 software. The systems to be investigated are Ti-O, Ta-O, Na-Ta-O, Nb-O and Zr-O. The measurements started with commercial TiO_2 powder samples. The PDFs generated for commercial TiO_2 powders are given in Fig.1a. The experimental PDF are compared to the simulated PDF curves of anatase and rutile. Then the samples synthesized by the direct injection method were measured. In order to examine the effect of UV light on the structure, also samples synthesized in the absence of UV light were prepared (*ex situ* samples). Some of those samples were treated under UV light. The PDF data for the ex situ samples were collected as well and their PDFs were compared to the products of direct injection method, Fig.1b. It is known that under UV irradiation photogenerated electrons reduce Ti^{4+} to Ti^{3+} which forms defect states of the band structure[3]. It is also known that in absence of irradiation the lifetime of Ti in 3+ oxidation state is limited to hours. However, according to some literature reports this lifetime can go up to months. Therefore these previously synthesized samples with and without UV irradiation were subjected to local structure analysis.

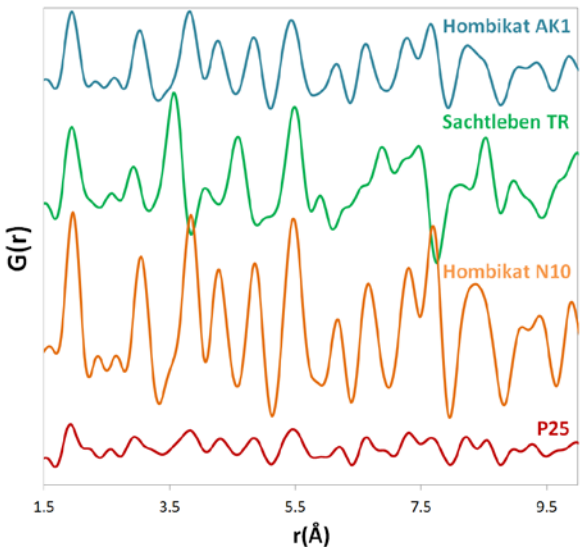

Fig.1a. PDFs of crystalline TiO_2 powders. Hombikat AK1 consists mainly of anatase, Sachtleben TR consists of rutile, P25 and Hombikat N10 are mixtures of anatase and rutile structures.

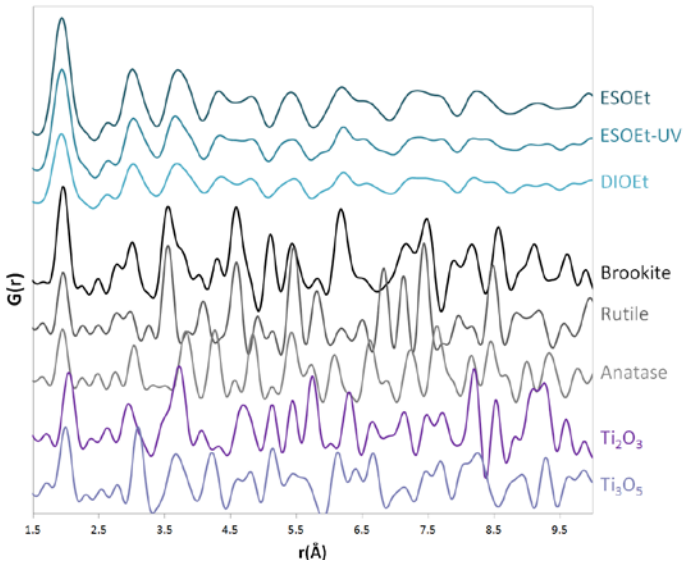

Fig.1b. Comparison of PDFs obtained for TiO_2 samples synthesized *ex situ* with UV light irradiation and via direct injection method with calculated PDFs of the polymorphs of TiO_2 and different titanium oxides.

In order to understand how the formation of the different crystal structures and their crystallinity were affected by the amount of injected precursor, PDFs of two samples were studied. One sample was prepared with 2.5 mmol of precursor while the other sample was formed by injection of 5 mmol of precursor. The experimental PDFs are shown in Fig.2.

In addition the influence of different Ti alkoxide precursors (titanium ethoxide, -butoxide and -isopropoxide) on the products was studied. A difference in the local structures among samples synthesized with different precursors could not be observed.

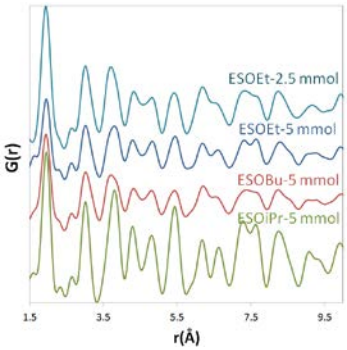

Fig.2. PDFs obtained for TiO_2 samples synthesized using different precursor concentrations and precursor compositions.

In case of tantalum oxide, samples with different injection times were analysed. The measured PDFs (Fig.3a) were compared to the PDF simulated for crystalline Ta_2O_5 as a reference. For the Na-Ta-O samples, the measured PDFs are shown in Fig.3b. were obtained. It is observed that in the absence of NH_3 during the synthesis the Na-Ta-O structure resembles that obtained from direct injection of only $Ta(OEt)_5$.

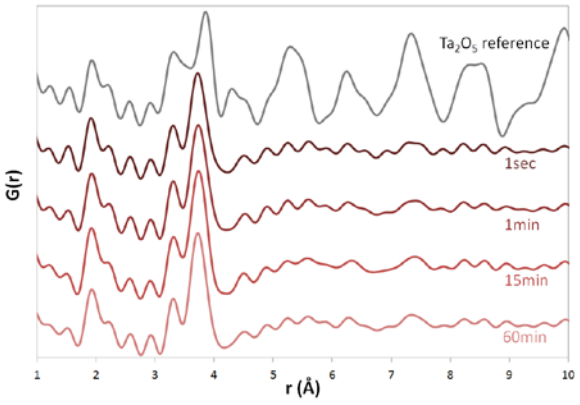

Fig.3a. PDFs obtained for Ta_xO_y samples synthesized with different injection times of the precursor vs. reference Ta_2O_5.

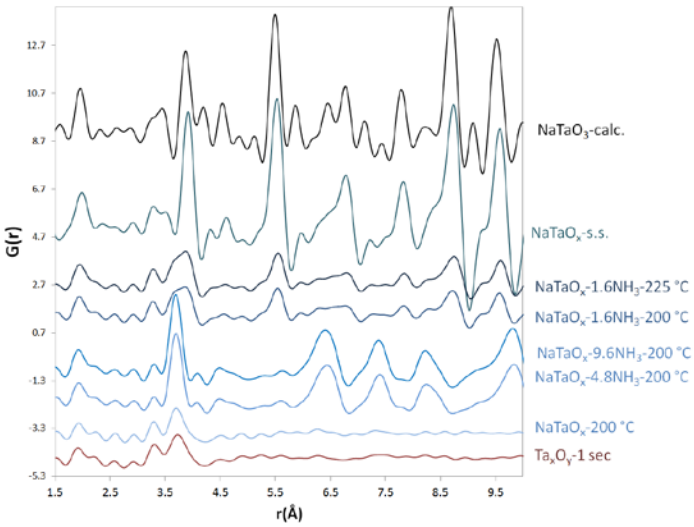

Fig.3b. PDFs obtained for $NaTaO_x$ samples synthesized under different conditions vs. reference $NaTaO_3$[4]. Amounts of NH_3 used in the synthesis are in mL. The PDF for Ta_xO_y (injection time of 1 sec) is added for comparison.

The powders obtained from the experiments with $Nb(OEt)_5$ and $Zr(OEt)_4$ precursors were also measured. In addition, oxides form the combinations of different metal ethoxides were synthesized. The PDFs are given in Fig.4a and b.

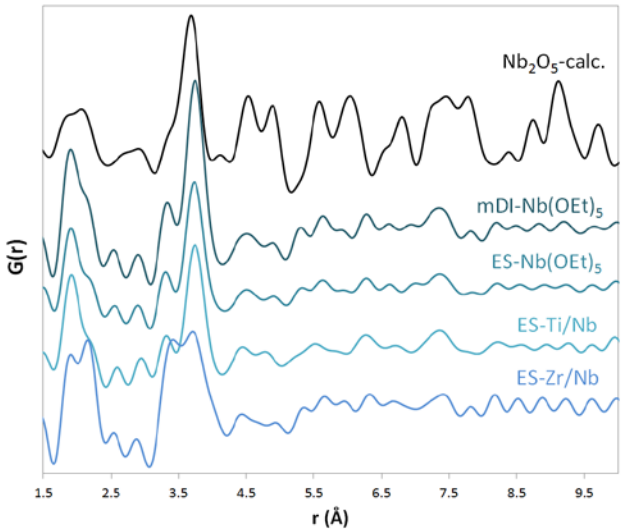

Fig.4.a. PDFs obtained for Nb_xO_y samples synthesized by the direct injection (mDI-$Nb(OEt)_5$) and *ex situ* methods (ES-$Nb(OEt)_5$). The figure shows also the PDFs of *ex situ* synthesized Ti/Nb and Zr/Nb mixed oxides. ´m´ denotes mixing the precursor in methanol before injection.

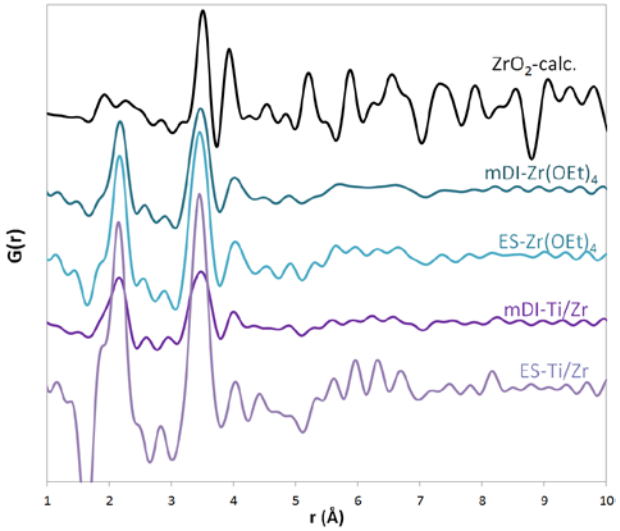

Fig.4.b. PDFs obtained for ZrO_x samples synthesized by direct injection (mDI-$Zr(OEt)_4$) and *ex situ* methods (ES-$Nb(OEt)_5$). The figure shows also the PDFs of Ti/Zr mixed oxides synthesized by *ex situ* and direct injection methods. ´m´ denotes mixing the precursor in methanol before injection.

So far, all collected data have been processed and qualitatively analysed. The future work requires detailed refinement of the local structures in order to relate catalytic activity and local structure properties.

References

[1] Grewe, T., Tüysüz, H., *Chemsuschem*, **2015**, 8, 3084-3091.

[2] Juhás, P., Davis, T., Farrow, C. L., Billinge, S. J. L., *J. Appl. Cryst*., **2013**, 46, 560–566.

[3] Chen, X., Liu, L., Yu, P. P., Mao, S. S., *Science*, **2011**, 331, 746-750.

[4] Ahtee, M., Unonius, L., *Acta Crystallographica A*, **1977**, 33, 150-154.