

The CAT-ACT Beamline at ANKA: A new high energy X-ray spectroscopy facility for CATalysis and ACTinide research

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The CAT-ACT Beamline at ANKA: A new high energy X-ray spectroscopy facility for CATalysis and ACTinide research

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Abstract. A new hard X-ray beamline for CATalysis and ACTinide research has been built at the synchrotron radiation facility ANKA. The beamline design is dedicated to X-ray spectroscopy, including ‘flux hungry’ photon-in/photon-out and correlative techniques with a special infrastructure for radionuclide and catalysis research. The CAT-ACT beamline will help serve the growing need for high flux/hard X-ray spectroscopy in these communities. The design, the first spectra and the current status of this project are reported.

1. Introduction

Synchrotron radiation based techniques have become key speciation methods in actinide [1] and catalysis research [2,3]. In the field of actinide research reliable radionuclide speciation techniques are important to characterize, e.g. geochemical processes such as mobilization/immobilization of long-lived actinide and fission product nuclides to assess long-term safety of the disposal of nuclear waste. The increasing need to understand degradation processes of nuclear waste forms such as discharged reactor fuel and vitrified reprocessing residues during extended interim storage demands the development of speciation methods capable of the direct characterization of highly radioactive samples with a minimum of pre-treatment. In this context standard X-ray absorption spectroscopy (XAS) and advanced high resolution X-ray emission techniques have been recently shown to be well suited to study the chemical state and electronic structure of radionuclides in various matrices - a prerequisite for predicting their reactivity [1,4,5]. For catalysis research in-situ and operando X-ray based characterization methods emerged as key elements for the rational design of heterogeneous catalysts [2,6-8]. This approach was not only appreciated by the scientific community, but also applied by industry, e.g. Haldor Topsøe A/S as one of the pioneering companies in Europe ([6] and refs therein). Knowledge of oxidation state, coordination environment, and nanoparticle morphology contributed significantly to deeper understanding of heterogeneously catalyzed reactions and serves today as a basis for the design of new catalysts and for first-principles kinetic modeling. At the Karlsruhe Institute of Technology a new hard X-ray beamline for CATalysis and ACTinide research at the ANKA synchrotron has been installed and commissioned and will be operated in close collaboration with ANKA scientists by the two KIT communities having essential expertise in these two application fields. The beamline design places emphasis on XAS in terms of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) combined with



'flux hungry' photon-in / photon-out techniques like X-ray emission spectroscopy (XRES), X-ray diffraction (XRD) and further correlative spectroscopies (infrared spectroscopy, IR, UV-vis spectroscopy), including gas analysis (mass spectrometry, on line IR, GC-analysis) in catalytic studies. Special infrastructure for experiments with radioactive samples and catalytic studies under reaction conditions is currently underway. The CAT-ACT beamline will help serve the growing need for high flux / high energy spectroscopy, complementing strongly overlooked existing beamlines in these fields.

2. Beamline layout and characteristics

Figure 1 shows the main components of the CAT-ACT beamline with a superconducting multipole wiggler (2.5 T, $K=11.2$, 15 mm vacuum gap, 10.2 keV critical photon energy, 4.7 kW radiated power), two mirrors for beam collimation, focusing and rejection of higher harmonics (vertically collimating Si mirror coated with Rh and Pt stripes and toroidal focusing mirror with Rh and Ir stripes) and a double crystal monochromator with Si(111) and Si(311) crystal pairs (fixed-exit, LN₂ cooled crystals, direct drive goniometer with maximal speed of 4°/s). The components are designed to provide high intensity (flux $\sim 10^{13}$ - 10^{14} photons/s/100 mA) in a wide photon energy range (3.1-60 keV) at fixed positions (beam size with mirrors $\sim 1 \times 1$ mm, mirrorless operation above about 35 keV) at two end stations (CAT and ACT) in two separate experimental hutches, built in series.

The wiggler source gives access to K absorption edges of heavy elements like Rh, Pd, Ag and Ce (of particular interest for catalysis research) and f-element actinide L₁-edges and lanthanide K-edges up to Gd, while the low energy limit of the beamline still allows investigations at the K-edges of transition metals and actinides M_{4,5}-edges. Compared to ANKA bending magnet radiation, the photon flux at 20 keV will be about two orders of magnitude higher, which is especially beneficial with respect to the spectroscopic sensitivity for dilute sample systems, e.g., for studying catalyst promoters or poisons or trace concentrations in environmental radionuclide studies.

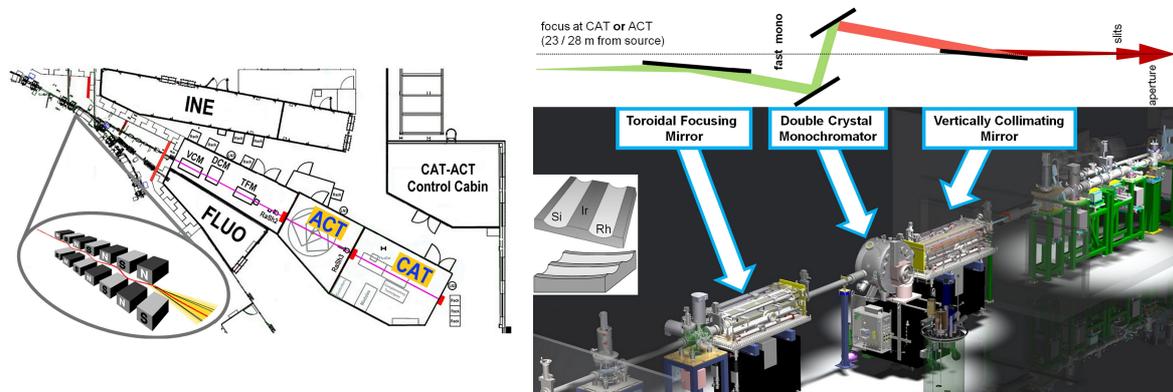


Figure 1. Layout of the CAT-ACT beamline at ANKA with two in-line experimental stations (left). CAT-ACT optical components designed and manufactured by FMB Oxford (Oxford, United Kingdom). From right to left: frontend components (intensity absorber, X-ray beam position monitor, white beam slit), collimating mirror, double crystal monochromator, diagnostics module, toroidal focusing mirror, beam shutter separating ACT hutch from optics section. Inset: focusing mirror coating scheme.

3. Experimental hutches

The CAT-ACT beamline comprises two alternately operated experimental stations. The ACT experimental hutch will be operated by KIT-INE as a temporary controlled area with the necessary infrastructure for handling radioactive samples, adhering to the double containment concept established at the ANKA INE beamline [9] to safely enclose all radioactive materials by two independent layers of protection. Measurements of non-fissile radionuclides with activities up to 10^6 times the European exemption limit and 200 mg of fissile U-235 or Pu-239 will be possible. The experimental infrastructure includes standard equipment for XAS measurements in transmission and

fluorescence detection mode, as well as a multi analyzer crystal high resolution X-ray emission spectrometer as central component. The latter has already been designed and commissioned at the INE beamline. Equipment for diffraction techniques (high energy X-ray scattering and single crystal X-ray diffraction) are envisaged as possible future upgrades.

The CAT experimental station will be operated by KIT-ITCP and KIT-IKFT and equipped with a special infrastructure for in-situ and in-operando catalytic studies, including supply of reactive gases. A number of specially designed sample environments for catalytic experiments under realistic reaction conditions in gas phase, at high pressure, high temperature or in liquid phase have been set up. They are presently complemented by further, more demanding set-ups for combining XAS with complementary characterization techniques (e.g., infrared spectroscopy and X-ray diffraction). They will allow to analyze the local molecular environment and the long range order structures of catalytically active materials and to study adsorbed reaction species simultaneously.

4. Project milestones

In 2011 the ANKA experimental hall was extended to accommodate the CAT-ACT experimental hutches and the control cabin. The superconducting multipole wiggler, designed and built by Budker Institute of Nuclear Physics (Novosibirsk, Russia), was installed into a short straight section of the ANKA storage ring in July 2014. The frontend beamline section built by FMB Berlin (Berlin, Germany), containing diagnostic elements and white beam slits, the radiation protection hutches comprising three separate sections (one for optics and the two end stations, ACT and CAT) and the lock room providing controlled access to the ACT station were installed shortly afterwards. The optical components were designed and installed inside the optics hutch in 2015 by FMB Oxford (Oxford, United Kingdom). Currently the commissioning of the optics components, implementation of the control system and integration of the CAT-ACT beamline into the personal safety and radiation protection system at ANKA are in progress. Installation of special infrastructure for actinide and catalysis research will be finished in the middle of 2016.

5. First results

Pilot experiments with synchrotron light were successfully conducted after the first commissioning phase in 2015 and first XAS spectra of samples relevant for both scientific fields were measured.

Research at ITCP and IKFT is focused on catalysts for energy related applications (solar fuels, conversion of biomass platform molecules), selective oxidation, sustainable fine chemical processes and exhaust gas purification. Figure 2 shows Pt L_3 -edge XAS spectra of two differently treated diesel oxidation catalysts which have been subject of intensive research [10,11], along with the spectrum of a Pt foil. The catalysts were prepared by incipient wetness impregnation of γ - Al_2O_3 , dried, calcined and reduced in 5% H_2/He ("fresh" catalyst) and then aged by mild hydrothermal aging procedure ("aged" catalyst). Spectra were measured in transmission mode using ionization chambers. The quality of the spectra shows already at this stage the endstation's potential for future studies in catalysis. They furthermore reveal the Pt particles are more reduced after ageing as a result of particle sintering during aging (reoxidation of small Pt-particles in air is faster for the small freshly reduced Pt-particles).

One of the major aspects of research performed at INE is the incorporation of nuclear fuel reprocessing residues (i.e., highly radioactive waste concentrates, 'HAWC') in specially designed glass matrices - a key step in immobilizing and conditioning separated minor actinides and fission products prior to their transport and final disposal. Nuclear waste glass simulants are investigated to optimize miscibility and radionuclide loading capacities of glass formulations used in a real industrial process. Figure 3 depicts the first U L_3 -edge XAS spectra recorded at CAT-ACT. The red curve shows the spectrum of a borosilicate glass doped with 4.7 wt.% UO_2 , prepared under oxidizing conditions at 1200 °C in a Pt crucible [12]. Comparison to the spectrum of uranyl ($(O=U^{VI}=O)^{2+}$) species present in the mineral meta-schoepite (blue curve) unambiguously proves that uranium in the glass is oxidized to the hexavalent state during the melting process.

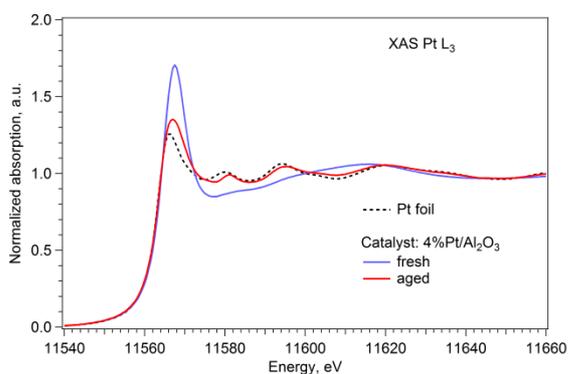


Figure 2. Pt L_3 -edge XAS spectra of freshly prepared and aged 4%Pt/Al₂O₃ diesel oxidation catalysts measured in transmission mode at CAT-ACT. The spectrum of a Pt foil was measured as reference and for energy calibration and is shown for comparison.

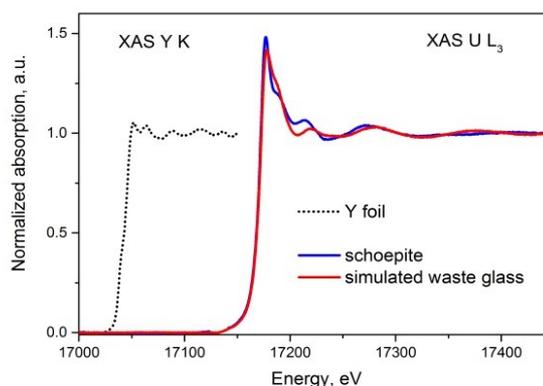


Figure 3. U L_3 -edge XAS spectra of U(VI) or ‘uranyl’ species in the mineral meta-schoepite (UO₃ · nH₂O) and a simulated U-borosilicate nuclear waste glass (4.7 wt.% UO₂ loading). Y metal was measured as energy calibration standard.

6. Acknowledgement

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