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The potential of ion beams for characterization of metal–organic frameworks

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ABSTRACT

Ion scattering has been employed for depth-profiling of metal–organic frameworks (MOFs) to characterize the degree of post-synthetic uptake of [FeFe](mcbdt)$(CO)_6$ (mcbdt = 2,3-dithiolato-benzoic acid). The system investigated consisted of UiO-66 (UiO = University of Oslo) MOF thin films grown on p-type Si wavers in which a molecular proton reduction catalyst [FeFe](mcbdt)$(CO)_6$ was introduced by postsynthetic exchange (PSE). We have characterized samples by Rutherford Backscattering spectrometry (RBS), Time-of-Flight Elastic Recoil Detection analysis (TOF-ERDA) and by Time-of-Flight Medium Energy Ion Scattering (TOF-MEIS). The beam induced sample modification during the analysis has been characterized by Scanning Electron Microscopy (SEM). No detectable sample modification was found for RBS and TOF-MEIS whereas TOF-ERDA had a clear impact in the present experiment. Composition profiles could be obtained and indicated enrichment of catalyst and/or catalyst residual near to and at the sample surface.

1. Introduction

Metal–organic frameworks (MOFs) feature unique capabilities in the field of catalysis due to their chemical versatility and extraordinary high surface area [1]. The molecular nature of MOFs allows the incorporation of molecular catalysts which results in new materials that can exhibit increased catalytic reactivity and stability. In this context, it is of great interest to characterize the distribution of catalysts within a MOF. The low density and the organic character of MOFs, however, make them a challenging substrate for depth profiling, and substantial sample damage is expected for a number of commonly used composition depth profiling methods.

Ion Beam Analysis (IBA) represents an interesting alternative since the different methods are typically referred to as almost non-destructive for common solid target materials and free from matrix-effects (see [2] for an overview of available standard ion beam methods for materials characterization).

Of the standard IBA-methods in particular particle-induced X-ray emission (PIXE) has been applied successfully for organic [3] and biological samples [4] but depth resolution is limited. Also micro-beam approaches have been successfully employed for characterization of delicate samples and even for irradiation of living cells [5] but complex preparation routines of the measurements limit application as a standard characterization method for multiple samples on short time-scales. Finally also secondary ion mass spectrometry (SIMS), particularly using the time-of-flight technique (TOF-SIMS), although no longer non-destructive, is available for characterization of sensitive organic materials [6]. Recently, the use of MeV ions in SIMS [7] has shown particular capabilities for analysis of especially macromolecule distributions [8]. All, the presented approaches are found highly sensitive, however, they also are more focused on small spot analysis and show some limitations in terms of sample throughput.

Thus, the use of elastic scattering of ions with energies of several ten up to hundreds of keV per atomic mass unit represents a simple straightforward approach with high-throughput which can be useful for characterization of MOF systems as well as their individual synthesis and fabrication steps, its application is at present however limited to only few investigations [9]. Even if being less sensitive than the methods stated above classical Rutherford Backscattering Spectrometry (RBS) measurements have shown being capable to quantify metal concentrations in organic matrices with no or only low impact on composition [10].

In the present work we investigated a number of MOF thin films using IBA-tools (RBS & Time-of-Flight Elastic Recoil Detection Analysis – TOF-ERDA) and Time-of-Flight Medium-Energy Ion Scattering TOF-MEIS. The investigated materials were crystallites of

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UiO-66 (UiO = University of Oslo) that contained a post-synthetically incorporated molecular proton reduction catalyst [FeFe](mcbdt)(CO)$_6$ (mcbdt = 2,3-dithiolato-benzoic acid) [11] grown on p-type Si-wafer substrates and fluorine doped tin oxide (FTO). We have employed ion beam based methods to characterize the depth distribution of the diiron complex. We discuss the quality of the information obtained from the individual methods and limitations in the application based on sample structure and composition.

2. Experiment and sample preparation

Silicon substrates (p-type [1 0 0]) were cleaned for 30 min at 80 °C with Piranha solution (3:1 vol. concentrated H_2SO_4:30% H_2O_2), rinsed with water and dried under a stream of air. FTO substrates (7 Ohm/sq) were prepared by sequential 10 min sonication in Alconox cleaning solution, water, ethanol and acetone. Thereafter the FTO samples were placed into a vial containing 1 mM terephthalic acid in dimethylformamide (DMF) for at least 12 h prior to the MOF thin film synthesis to form a self-assembled monolayer. The substrate choice of FTO (in contrast to the, in terms of scattering kinematics, more favorable Si) was made to be able to provide electrical contact.

For the MOF synthesis, benzoic acid was dissolved in DMF, $ZrCl_4$ was added to the solution and sonicated before a small amount of water was added. It was transferred into a volumetric flask to give a concentration of 1.84 M (benzoic acid), 25 mM ($ZrCl_4$) and 125 mM (H_2O), respectively. The solution (6 ml) was filled into screw-vials and pre-treated at 80 °C for 2 h. Then 2 ml of a terephthalic acid stock solution (75 mM) was added and the substrates were placed tilted at *ca.* 45° into the vials. The conductive side of the FTO and the polished side of the silicon were facing downwards. The vial was allowed to react solvothermally at 120 °C in a sand bath in an oven for 24 h. After cooling down to room temperature (20–30 min), the film was rinsed with DMF and incubated in DMF for 24 h. Then the solution was changed to methanol for another 24 h. The diiron complex [FeFe](mcbdt)(CO)$_6$ (41.3 mg, 0.1 mmol) was dissolved in deoxygenated methanol (2 ml) by sonication for *ca.* 20 min. The insoluble residue was removed by centrifugation. The UiO-66 thin film sample was placed inside the vial with the film side upwards for 24–72 h at room temperature. Afterwards, the film was washed for three times with methanol, each time 24 h.

The RBS and TOF-ERDA experiments were performed employing a 5 MV 15SDH-2 Pelletron tandem-accelerator at the Ångström laboratory. By the use of different ion-sources beams of many different ion species with energies in the range of 2–50 MeV can be produced. In the present study 2 MeV $^4He^+$ ions (for RBS) and 32 MeV $^{79}Br^{7+}$ as well as and 36 MeV $^{129}I^{8+}$ ions were used (TOF-ERDA). The scattering chamber with a base-pressure of $<1 \times 10^{-5}$ Pa holds a solid state detectors for RBS, in Cornell geometry, situated at 170.0° scattering angle. A time-of-flight tube situated at 45° scattering angle holds two time-detectors based on electrons emitted due to ion transmission through a thin C-foil and being detected by a MCP stack after deflection [12] as well as a final solid state detector. The set-up thus permits to perform $\Delta t/E$ coincidence measurements of scattered and recoiled particles. A detailed description of the set-up and its characteristics is given elsewhere [13].

TOF-MEIS experiments have been performed using a system based on a 350 kV Danfysik implanter [14]. A large solid-angle (120 mm diameter located 300 mm from the sample position) position sensitive detector permits to record time-spectra at very low primary particle doses on the order of 10 nC per spectrum. Relative energy resolutions of $\delta E/E$ of about 0.01–0.02 can be achieved with the present system yielding a maximum depth resolution of better than 2 nm for typical bulk systems [15].

SEM images of the sample were recorded using a Zeiss Merlin equipped with a Schottky field emission gun. The sample charging was reduced by sputter-coating the targets with Au/Pd prior to the measurement.

3. Results and discussion

3.1. TOF-ERDA

Initial TOF-ERDA experiments were performed on samples consisting of multilayers of crystallites loaded with the catalyst and deposited on FTO [16]. Since significant losses of light elements have been observed in similar experimental approaches [17], we compare experimental spectra for a single sample at two different fluences. Primary beam doses differed by a factor of 10 and were estimated to be 6×10^{10} and 6×10^{11} ions/cm^2 from the primary beam currents of about 0.5 nA as well as from the geometry and necessary particle flux in the evaluation. Evaluation was done using the CONTES software package [18]. While the TOF-ERDA data in principle yields depth-resolved elemental composition profiles, no significant gradient in elemental concentrations was observed in the obtained spectra. As a main feature, the Fe to S ratio was found to be close to 1:1 as expected for an intact catalyst present in the sample. Also the Zr concentrations which are found about 6 times higher than the Fe and S concentrations is in reasonable agreement with the sample preparation procedure. The relative concentrations of C and O, however, are found to deviate strongly from expectations according to the stoichiometry of the MOF. The depletion in C and the relative increase in O can be interpreted by erosion of the MOF-crystallites and increasing signal from the FTO substrate featuring higher oxygen content. Additionally, close to the surface (according to the energy of the recoiling particles) the Fe concentration exceeds significantly the measured S concentrations for higher particle fluence, while the opposite is observed for lower dose. Note, however, that for the lower dose statistics is still found poor. The observed significant depletion in C is in agreement with a more comprehensive study by Giangrandi et al. [17] who observed 25% depletion in C for similar total energy deposition. The higher loss in the present study may be attributed to the higher stopping power of iodine (about a factor of 2) compared to the Cl ions used in the referred study.

Complementary SEM-measurements showed that, indeed during the TOF-ERDA measurement the sample structure was severely deteriorated (see insets in Fig. 1). The nature of the induced damage remains yet unclear and might be due to both, high thermal loads on the sample (non-local) as well as local disruption of the structure due to the high energy loss of the probing ion species (several keV/nm).

As becomes apparent from the SEM-pictures the samples exhibit a high degree of surface roughness (on μm length scales). This roughness, in combination with the rather grazing incidence and exit angles (22.5°) employed in TOF-ERDA clearly represents a severe obstacle for quantitative depth-profiling even if sample decomposition during experiments could be avoided. Complex trajectories penetrating multiple crystallites at e.g. position close to their edges can be expected and will severely deteriorate depth scales. This difficulty is expected to persist even if only single crystallites with sub-monolayer surface coverage are grown. Thus, TOF-ERDA, especially when using heavy probing ions, can be ruled out as a straight forward method for depth-profiling of the present highly crystalline system unless almost complete monolayer films of crystallites are grown.

For samples with homogeneous catalyst distribution, however, TOF-ERDA is still expected to be a powerful and relevant tool. Also,