Energy dispersive x-ray absorption spectroscopy for studies of catalysts in solution

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Abstract. The millisecond time resolution achieved by Energy Dispersive EXAFS (EDE) and the high stability provided by the unmoved optical components make this technique very attractive to study chemical reactions and elucidate reactive intermediate species. Great progress has been made on the EDE study of the problematic in situ experiments of reactions in solution. Herein, limitations and solutions for the study of these systems are given. Two examples of catalytic reactions followed in situ and carried out in a stopped-flow/UV-Vis spectroscopy/EDE set-up are shown.

1. Introduction
Energy Dispersive Extended x-ray absorption spectroscopy (EDE) is very well suited to follow chemical reactions in time at the millisecond, or even at the microsecond, range in a single shot experiment. This type of experiments potentially allows probing the local structure and the electronic state of short lived intermediate species, as well as following the kinetics of the reaction. Therefore, direct structuro-kinetic correlations can be drawn. The experiments take advantage of the stability of the dispersive set-up given by the beamline’s optical elements during acquisition.

2. EDE experiments of reactions in solution
Even though reactions in solution could seem to be straightforward to study by EDE, because they profit from the intrinsic advantage that samples are spatially homogeneous and can give rise to very good quality of data, the reality is another and very different, where many other factors -which will be listed below- should be taken into account. As a result, only about 5% of the experiments carried out
on an EDE beamline of a high-flux third-generation synchrotron source investigate chemistry in
solution; and this is reflected in the number of publications of this sub-genre. Nonetheless, if an EDE
experiment of samples in solution is done consistently, and if all critical factors that can disturb the
experiment are taken into account, the actual spectral changes can be legitimately and unambiguously
correlated to the real chemical structures and kinetic data.

It is common to find that spectral changes of reactions in solution are subtle and the EXAFS
oscillations are very much reduced because of the highly disordered environment in liquids.
Consequently, these changes are difficult to observe as real structural or electronic variations. For this
reason, the x-ray beam must be monitored and the high stability of the beam assured. Also, the optical
components should be maintained free of vibrations, and free of mechanical and temperature
variations. Evaluation of the noise level should be carried out carefully so to discriminate any
perturbation from real spectral features. Because of this trait very often only near edge spectra
information (XANES) can be recorded. Therefore, qualitative and quantitative XANES analysis
becomes very important. Principle Component Analysis (PCA) methodologies can be decisive in
discerning short-lived intermediate species. Additionally, algorithms such as MXAN code [1] can
quantitatively elucidate the structure of compounds in situations where good quality EXAFS data
cannot be obtained.

Another typical phenomenon occurring in EDE experiments of solution reactions is precipitation
and partial insolubility of the species. These effects are a direct consequence of the nature of EDE
experiments, which can only be carried out in transmission mode and therefore, the concentration of
the compounds need to be relatively high. On the other hand, experiments in fluorescence mode have
been able to be performed on the dispersive EXAFS beamline of the European Synchrotron Radiation
Facility (ESRF), ID24, using the Turbo-XAS mode [2]. However, the current available set-up for
homogeneous systems is not yet fully optimized to carry out fluorescence Turbo-XAS experiments at
a time resolution of a few hundredths of milliseconds.

For this reason we have spent much of the efforts in mastering the way to collect I0 and I1 in a
dispersive EXAFS experiment in transmission both for solid and liquid samples [3]. If this is achieved,
EXAFS data can be obtained even in fairly dilute solutions without losing spectral information. This
aids the posterior background subtraction and normalization of the experimental data that can be
readily performed, thus resulting in data free of artifacts. For example, in a stopped-flow experiment
that uses the exact environment – in this case a cuvette with vitreous C windows- to measure I0
(solvent) and I1 (compound dissolved in solvent) we can obtain measurable (EXAFS) concentrations
of KReO$_4$ in water down to as low as 8 mM. This is very important as homogeneous catalysis it is
often the case that the systems of real interest function best in the low millimolar range, if not lower.
Even if these experimental concentrations happen to be higher than real catalytic concentrations, the
subsequent reaction mechanisms are more likely to be extrapolated to what occurs in reality. This
statement though, should unquestionably be always verified by concentration variation experiments
made either offline, or preferably online.

The last phenomenon, but not least important and often under-estimated, that complicates the study
of solution EXAFS experiments in high-flux third-generation sources is the effect of the x-ray beam
[4]. Mainly, the temperature increase caused by the x-ray beam impinging on a localized sample spot
can disturb the nature of the compound and reaction under study. Some of the variations that can
emerge from this heat load are: increase of reaction rates, redox behaviour, and destruction of active
sites, formation of radical species, formation of colloidal particles, radiolysis of water and formation
of bubbles. Since all these effects are very dependent on the composition and characteristics of each
system they need to be studied and checked on a case by case basis. It is then not surprising that the
combination of a secondary technique to the main XAS spectroscopy is not only useful for obtaining
complementary chemical and kinetic information but essential for cross-checking the reliability of the
spectral outcome.
As it has been mentioned, all these complications can be overcome with good experimental planning and a multiple-technique methodology. If additionally it is reinforced by theoretical chemical calculations, one leaves the legitimacy of the results to only the treatment and analysis of data.

3. Practical examples

Herein, two examples are shown: the oxidation addition process of iodobenzene to [(Ph₃P)₂Pd(dba)] (dba=dibenzylideneacetone) and the reaction of hypophosphorous acid with the CH₃ReO₃ catalyst. The experiments were carried out in a stopped-flow/UV-Vis set-up. This was synchronized at the millisecond range with the collection of data (FReLoN2k detector [5]) at the EDE beamline ID24 of the ESRF.

The first example concerns the oxidation addition of 10 eq. PhI onto 40 mM of [(Ph₃P)₂Pd(dba)] in toluene at 40°C [6]. This process is often the overall rate-determining step of the catalytic cycle involved in the formation of C-C and C-N bonds and is very important for major chemical industries. This reaction was followed by EDE at the Pd K-edge (24.350 keV) with a time resolution of 500 msec. The nature of the observed data was verified offline with UV-Vis experiments and we could conclude that catalyst concentrations ranging between 500 µM and 40 mM did not change the reaction. The noise level of the useful data obtained (XANES region) was carefully evaluated. Synchronous UV-Vis and EDE measurements, done with and without x-ray beam, allowed to evaluate its effect. The addition of iodine on the coordination sphere of the Pd catalyst was accelerated a factor of two under the presence of x-rays but did not change the reaction mechanism. Long exposure times though caused the formation of Pd clusters. DFT calculations (MPW1PW91) suggest that the final trans-[(PPh₃)₂PdPhI] product is formed via the intermediate cis isomer species, which has never been structurally elucidated in situ. MXAN has shown to be able to structurally discern between cis and trans isomers. However, the bulk nature of the XAS technique together with the very short-lived species makes this information difficult to extract. This is still a topic under discussion.

Other analogous Pd catalysts were also studied in the same way but they were broken apart and clearly damaged by the x-rays. These catalysts included combinations of [Pd(dba)₂] and [Pd(OAc)₂] with different equivalents of 2-biphenyl-di(tert-butyl)phosphine, 1,3-Bis(2,6-di-i-propylphenyl)imidazolium chloride and tricyclohexyolphosphine.

The second example is the polymerization of the methylrhenium trioxide (MTO) catalyst. A reaction of 20 mM of MTO with 1.6 mM of H₃PO₂ in water and acidic medium at 25 °C was investigated in situ at the Re L₃-edge (10.535 keV) in a 5x1 mm² cuvette in order to elucidate the presumed methylrhenium dioxide (MDO) short-lived intermediate species. MDO is thought to play an important role in many reactions where MTO acts as an oxidizing catalyst. The reaction was followed during 90 sec with a time resolution of 150 msec (see figure 1). Longer reaction times under beam condition caused the precipitation of the insoluble polymeric Re compound. By using the FITIT 2.0 software, that includes algorithms combining principle component analysis (PCA) of the experimental data, multidimensional interpolation of XANES as a function of structural parameters, and ab initio XANES calculations, the structure of the reactant dissolved in water could be uncovered, which fitted well with the results obtained from EXAFS analysis, and the transient MTO species could be elucidated and characterized structurally [7].
In conclusion, this paper shows the complexity of time resolved EDE experiments of reactions in solution. Problems arising from the effect of the beam and the nature of a dispersive XAS experiment can be overcome by using good working methodologies, complementary and cross-checking techniques and, if possible, being accompanied with theoretical calculations. In this way the validity of the results can be assured. Two working models herein described exemplify the scope of this sort of experiments, this being interesting for elucidating structuro-kinetical data of compounds and reactions that may involve short-live intermediate species.

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Figure 1. Experimental time-resolved Re L\textsubscript{3}-edge XANES spectra measured during polymerization reaction of MTO. The integration time of the spectra is 150 msec. A step in time between the spectra is 9 sec. Insert: Embedded error function (IE) used to determine the number of observed spectral components within the FitIt 2.0 software [7].

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