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Application for beam time at ESRF – Experimental Method

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Aims of the experiment and scientific background

The Fenton reaction, a well-known oxidation methodology widely applied to degrade organic pollutants not easily removable, involves the generation of highly oxidant hydroxyl radical by the conjunction of iron ions and hydrogen peroxide. The reaction is a catalytic process, where the reacted Fe^{3+} is converted to the initial Fe^{2+} by hydrogen peroxide. This process requires a strict pH control, as slight shifts towards the alkaline range favour the growth of iron oxohydroxycomplexes avoiding further application of the catalyst. In addition, this secondary process generates sludges that have to be managed later on.
In this framework, the immobilization of Fe into different materials has been proposed (Noorjahan et al, 2005; Ruda et al, 2005) to prevent the precipitation of Fe whilst keeping the catalytic capacities of Fe in the Fenton reaction. The immobilization of Fe, and the possible reuse of these materials several times, represents a clear environmental and economic improvement. In this context, our research group has been working since 2004 in the development of effective heterogeneous catalyst, adsorbing iron onto different materials such as zeolites or clays.

Iron can be exchanged into several types of cavities inside the zeolite framework, as it known to occupy inter-layers positions in the clay mineral but also adsorbed onto the mineral surface. In the context of a Fenton reaction, where iron is introduced in the system by a zeolite, the coordination sites, oxidation state and molecular environment of the iron present in these materials, are expected to strongly influence the catalyst properties. In order to achieve a better understanding of the Fenton reaction in these specific catalytic systems (with iron encaged in a nonreactive material), the main objective of this study refers to the characterization of iron catalyst by EXAFS and XANES techniques. This characterisation will be conducted both before and after the Fenton reaction taking place.

Our research group has more than seven years of experience concerning the application of synchrotron-based techniques to the study of environmental and biological samples. Seven projects have been already performed in the frame of HASYLAB (both beamlines A1 and L) (Bernaus et al. 2005; Bernaus et al., 2006) and ESRF (beamline ID26) synchrotron facilities. In addition, our research group keeps a close contact with three well-known investigation groups related to the application of synchrotron-based techniques, namely the Department of Environmental Science and Technology TUHH of Hamburg, the Department of Geological and Environmental Sciences at the Stanford University and the Environmental Sciences Department of Brookhaven National Lab in New York.

Experimental method

The study will be carried out with three types of zeolite Y, namely Ultra-Stable Y Zeolite (Zeolyst International), Zeolite Y (Grace Davison), clinoptilolite (the most common natural zeolite), and a clay with a high exchange capability (montmorillonite) loaded with either Fe^{2+} or Fe^{3+}. All the samples will be previously milled, sieved, homogenized with polyethylene and pressed as a pellet.

In order to assess the oxidation state of iron, a number of reference compounds ($Fe(NO_3)_3 \cdot 9H_2O$, $FeCl_3 \cdot 6H_2O$, $Fe_2(SO_4)_3 \cdot 9H_2O$, Fe_2O_3 and $FeSO_4$) will be also analysed during the beamtime. These reference compounds will be prepared following the same procedure described above for unknown samples.

The proposed experimental set-up at the beamline is:

- **Standard BM-25** beamline set-up for the Kα iron absorption energy (7112 eV): tuneable energy (7000-8000 eV) and fluorescence detector.
- Si (111) double crystal monochromator
- Software: deconvolution software for the on-line data treatment of complex samples

Laboratory set-up:
Press, fume hood and analytical balance.
All samples will be prepared in our own laboratories. Only in very specific cases the use of the ESRF chemistry laboratories will be required. The samples to be brought to ESRF are harmless, and therefore no specific safety measures are needed. Nevertheless, all samples and employed stuff will be brought back to our laboratories after the experiments.
No technical difficulties are expected.

Results expected

This project aims to evaluate the position, the coordination and the oxidation state of iron in the framework of different types of zeolites and one clay (montmorillonite). By determining the speciation and the distribution of Fe before and after the Fenton reaction, we expect to find a valuable knowledge to explain the different reactivity of the various zeolites. In this context, XANES and EXAFS can be used to determine the local coordination environment of iron, as well as their oxidation state, before and after their use in the Fenton reaction. The data obtained in BM-25 will be correlated with the Fe content of the samples before and after the Fenton reaction and with their different reactivity such as concentration of H_2O_2, organic matter and pH. Thus, the success of the project would be related to a major understanding of the role of the environment of both Fe^{2+} and Fe^{3+} in the Fenton reaction that would lead to an improvement of the reaction efficiency. Once the relationship between the environment and speciation of the iron catalyst with the Fenton reaction yield is known, the possibility to improve the system for more efficient and selective degradation of certain organic pollutants will be open.

References

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