

**Experiment title:**

XAFS studies of immobilized polymerization catalysts

Experiment number:

CH1485

Beamline:

BM29

Date of experiment:

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to:

18/7/03

Date of report:

25/2/04

Shifts:

6

Local contact(s):

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*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):****Martyn Pillinger*, Isabel S. Gonçalves*, João Rocha**

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Aims. In this experiment, X-ray absorption fine structure (XAFS) measurements were carried out in the solid-state for a series of tailored metal catalysts. The materials were prepared in advance by immobilisation of acetonitrile complexes of the type $[M(\text{CH}_3\text{CN})_n(\text{A})_2]$ [$M = \text{Cr}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$; $\text{A} = \text{BF}_4^-, \text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4^-, \text{B}(\text{C}_6\text{F}_5)_4^-$; $n = 4-6$] in porous hosts containing chelating nitrogen ligands. Two examples of the “solid ligands” used are given in Fig. 1. The objective of experiment CH1485 was to characterise the average local structural environments of the different metals in the synthesised materials using XAFS spectroscopy.

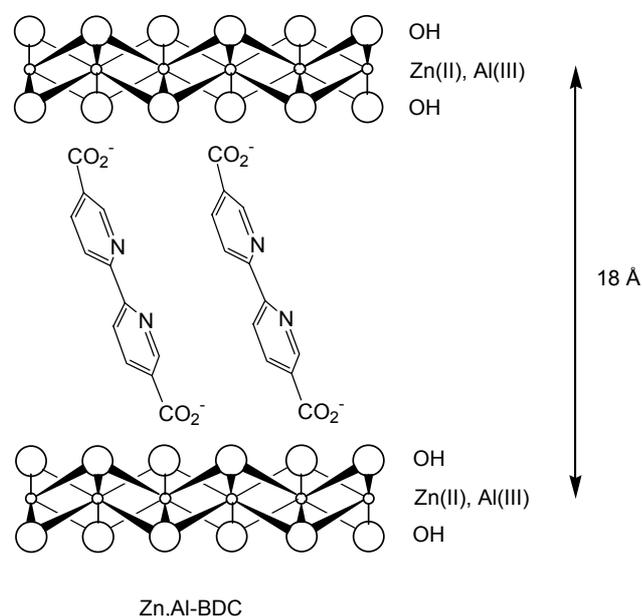
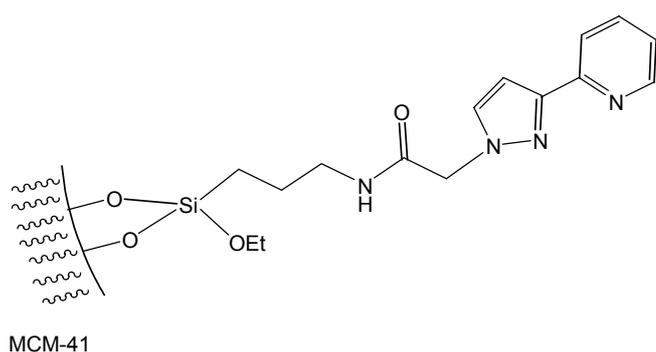


Fig. 1. MCM-41 derivatised with a pyrazolylpyridine ligand and a Zn,Al layered double hydroxide (LDH) pillared by 2,2'-bipyridine-5,5'-dicarboxylate (BDC) anions.

Experimental details. Cr K- (5.99 keV), Mn K- (6.54 keV), Ni K- (8.33 keV) and Zn K-edge (9.66 keV) X-ray absorption spectra were collected for samples in the solid state at 300 K and also at *ca.* 40 K (using an Oxford Instruments cryostat filled with He exchange gas) in transmission mode with ion chamber detectors on BM29, with the ESRF operating at 6 GeV in hybrid mode with typical currents of 170–200 mA. The order-sorting double Si(311) crystal monochromator was detuned by 40-50% to guarantee harmonic

rejection. Usually, scans were set up to record the pre-edge at 5 eV steps and the post-edge region in 0.025–0.05 Å⁻¹ steps (2s per step), giving a total acquisition time of *ca.* 45 min per scan. A total of about 40 spectra were recorded over the two days. About 6 hours beamtime was lost due to RF problems. Analysis of the results is ongoing, using the programs EXCALIB, EXBACK and EXCURVE (EXCURV98, Daresbury Laboratory, UK). Some results are reported here for the layered double hydroxide hosts.

The material Zn₂Al-BDC (Fig. 1) was prepared by ion-exchange starting from a Zn₂Al-NO₃ precursor with Zn/Al = 1.5. Three Zn···O and four Zn···M (M = Zn, Al) shells could be fitted to the low temperature Zn K-edge EXAFS of Zn₂Al-NO₃ (Fig. 2, Table 1), in accordance with a model for an ordered cationic sheet (Fig. 3). Peaks P1, P3 and P4 correspond to the first three O shells, while P2 and P5 to P8 are mainly caused by the metallic neighbors at a , $\sqrt{3}a$, $2a$, $\sqrt{7}a$ and $3a$ (where a is the cation-cation distance = 3.06 Å as determined by powder XRD), respectively, from the absorbing atom in the LDH layer.

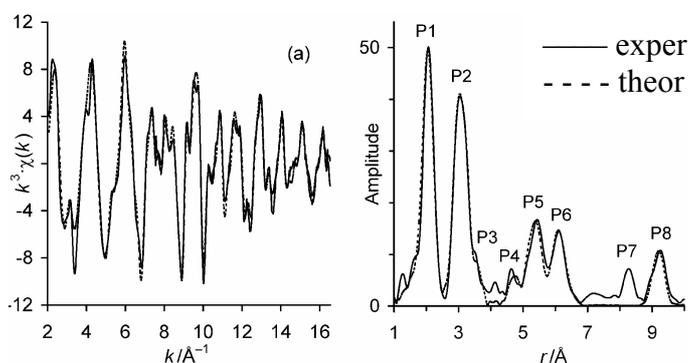


Fig. 2. Low temperature (40 K) Zn K-edge EXAFS and Fourier transform of Zn₂Al-NO₃.

Table 1. Zn K-edge EXAFS-derived structural parameters for Zn₂Al-NO₃

Shell	No. atoms	$r/\text{Å}$	$2\sigma^2/\text{Å}^2$
Zn···O (P1)	5.5	2.075	0.0118
Zn···Zn/Al (P2) ^a	6.0	3.059	0.0072
Zn···O (P3)	6.0	3.543	0.0172
Zn···O (P4)	12.0	4.776	0.0270
Zn···Zn (P5)	6.0	5.299	0.0121
Zn···Zn/Al (P6) ^b	6.0	6.139	0.0079
Zn···Al (P8)	6.0	9.192	0.0069

^a Mixed site: 0.47 Zn/0.53 Al.

^b Mixed site: 0.50 Zn/0.50 Al.

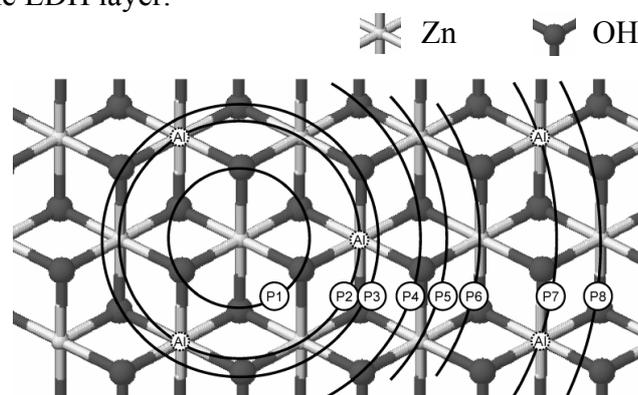


Fig. 3. Model of an ordered cationic sheet for a Zn₂Al-LDH with Zn/Al = 2.

Multiple scattering contributions were included for the linear unit comprising the shells at 3.06, 6.14 and 9.19 Å. The refined metal-metal distances are in good agreement with the expected values of a , $2a$ and $3a$, respectively. The Zn K-edge k^3 -weighted EXAFS spectrum of Zn₂Al-BDC was very similar to that for the Zn₂Al-NO₃ precursor, confirming that no significant disruption of the layer structure occurred during intercalative ion exchange of the dicarboxylate anion. Work is ongoing to analyse the XAFS results for the supported catalysts obtained after immobilisation of the MeCN complexes in Zn₂Al-BDC and also the derivatised MCM-41 materials.

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