



Experiment title: Methodological Study by Anomalous Diffraction of the Precise Location of two Cations In Zeolites Under Working Conditions

Experiment number:
02-02-610-a

Beamline: D2AM	Date of experiment: from: 11/06/03 to: 17/06/03	Date of report: 15/10/2003
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Introduction

The experiments reported here are part of a PhD thesis (H. Palancher) dedicated to the methodological study by anomalous diffraction of the precise location of cations in zeolites in the presence of multi-component adsorbed phases.

The industrial and scientific background is based on optimisation and development of new molecular sieves (such as X, Y or A zeolites) for high performance processes for separation and purification of hydrocarbon isomers. In such molecular sieves, adsorption properties and, more precisely, selectivity and capacity of adsorption can be correlated with the distribution of charge compensating cations.

Preliminary measurements performed at room temperature, with pre-treated (dehydrated) samples (SrX and SrRbX) sealed in capillary holders have shown the strong sensitivity of AWAXS to the distributions of cations (Sr^{2+} and Sr^{2+} or Rb^+ respectively) (see ref. [1]). Moreover a dedicated methodology (optimisation of the beam optics, the data collection strategy and the detection system) has been established.

To study *in situ* the variation of the cation distribution in the same samples under a variety of temperature and atmosphere compositions, an experimental set-up (based on ref. [2]) has been especially designed. Its first development has been used to characterise by *in situ* anomalous diffraction SrX at different steps of dehydration [3]. Then a new heating system providing a very low temperature gradient along the sample has been inserted [4]. This improved set-up has enabled high quality diffraction data collection on *in situ* dehydrated SrRbX [4].

AWAXS data refinement strategy has been developed on the dehydrated SrX sample data and its efficiency shown in the study of dehydrated SrRbX which is a particularly difficult case for X-Ray diffraction: Rb^+ and Sr^{2+} cations have the same number of electrons [4, 5].

The experiment number 02-02-610-a had three main aims. First, a study of cation distribution in SrX with water content so as to improve on the *ex situ* analysis of water saturated SrX. Second, investigation of the influence of cation size on cation distributions in bicationic samples with the degree of hydration by AWAXS *in situ* or *ex situ* measurements on NaRbX ($r_{\text{Na}^+} = 1.02\text{\AA}$ and $r_{\text{Rb}^+} = 1.52\text{\AA}$), and on CaSrX ($r_{\text{Ca}^{++}} = 1.00\text{\AA}$ and $r_{\text{Sr}^{++}} = 1.18\text{\AA}$) with analysis of competitive population of each site. Finally, we also performed tests by anomalous diffraction on dehydrated SrRbX under dynamic para xylene adsorption conditions. Cation distributions evolution due to hydrocarbon molecules adsorption has been followed.

Experimental set-up

The experimental set-up enables *in situ* diffraction and absorption studies in transmission mode on a powder sample held in a rotating glass capillary under controlled temperature and flushing gas of controlled composition (cf. fig. I). The gas can be charged with hydrocarbon molecules (para-xylene in this case), when it flows through hydrocarbon in liquid phase. A detailed description of the furnace and of the reaction cell can be found in ref. [6]. Identical experimental conditions were used for each *in situ* dehydration (dried N₂ used as flushing gas and sample temperature set at 250°C) until a stable state was obtained. Anomalous diffraction studies were performed at rubidium and strontium K absorption edges (respectively 15.202 and 16.106keV). High resolution diffraction patterns were recorded at two energies (10eV below considered edge and far below). For water saturated SrX, an additional dataset has been collected at intermediate energy (65eV below the Sr absorption edge).

Results

All diffraction patterns collected on a sample for given adsorption conditions were refined simultaneously using the Fullprof software package [7] with non constrained site occupancies. Preliminary results show the importance of the exchange of about 18 Sr⁺⁺ in SrX by 18 Ca⁺⁺ even if those cations have the same valence and very close ionic radii (cf. table 1). Indeed at highest hydration degree, only 27.8 Sr⁺⁺ cations per unit cell have been localised in SrX on sites I, I' and II whereas 39.7 cations are on these sites in CaSrX (non localised Sr⁺⁺ cations in SrX are very probably disordered in the supercage). On the other hand, Ca⁺⁺ and Sr⁺⁺ exhibit the same distributions on sites I, I' and II in CaSrX, to a first approximation, whatever the hydration level. When considering NaRbX, large differences between Na⁺ and Rb⁺ cation distributions are observed for the two hydration degrees (cf. table 2). Lack of time prevented us from performing AWAXS measurements at the Sr absorption edge on SrRbX dehydrated under para-xylene adsorption. However with data collected only at the Rb absorption edge, first refinements show interesting cation motions [8], which have to be confirmed. In conclusion, this experiment enabled us to characterise the influence of cation size on distributions in bicationic zeolites and to perform an *in situ* AWAXS study at Rb and Sr absorption edges.

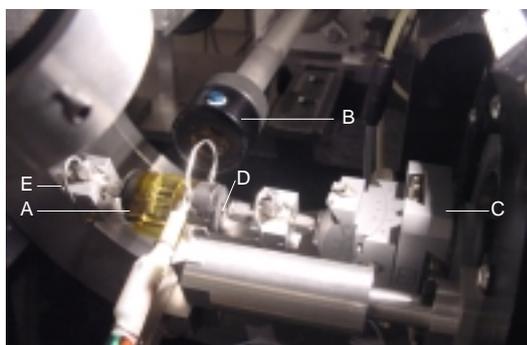


Fig. I: Newly developed cell mounted on BM2 goniometer [6]. Powder sample position (A) in incoming X-ray beam (B) can be optimised thanks to goniometer head (C). Temperature up to 250°C is obtained with cylindrical furnace (D). Capillary holder (E) enables sample rotations as well as gas admission and extraction.

		Site I		Site I'		Site II		Cation amount	
		Ca ⁺⁺	Sr ⁺⁺						
CaSrX	<i>In situ</i> dehydrated	3.3	4.9	4.9	7.6	10.6	10.7	18.8	23.2
	Water saturated	0	2.3	9.7	9.5	7.9	10.3	17.6	22.1
SrX	Water saturated		1.2		15.1		11.5		27.8

Table 1: Preliminary results concerning cation distributions in CaSrX (at two degrees of hydration) and in water saturated SrX.

		Site I		Site I'		Site II		Site III		Cation amount	
		Na ⁺	Rb ⁺								
NaRbX	<i>In situ</i> dehydrated	16.2	0	0	5.2	21	7.3	18.3	18.2	55	30.7
	Water saturated	7.0	1.1	15.1	1.7	6.4	26.5	16.2	0	44.7	29.3

Table 2: Preliminary results concerning cation distributions in NaRbX at two degrees of hydration.

[1]: experimental reports CH1216 and CRG 02-02-188-a, C. Pichon et al., 2002.

[2]: P. Norby, C. Cahill, C. Koleda and J.B. Parise, *J. Appl. Cryst.* (1998) 31, 481-483.

[3]: experimental report CRG 02-02-188-b, H. Palancher et al., 2002.

[4]: experimental report CH1327, H. Palancher et al., 2002.

[5]: J.L. Hodeau et al., *ECM (Durban- South Africa)*, 2003.

[6]: H. Palancher et al., *patent N° 03/07 641*, 2003.

[7]: J. Rodriguez-Carvajal, In: *Collected abstracts of Powder Diffraction Meeting*, Toulouse, France, 127 (1990).

[8]: proposal 02-02-636, 2003.