Experimental report

24/05/2019

Proposal:	**5-22-744**	**Council:**	4/2015
Title:	Location and Mobility of acidic protons in zeolite L by Neutron powder diffraction		
Research area:	Materials		

This proposal is a new proposal

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Samples: D9Al9Si27 O72
D9Al9Si27 O72*nD2O

Instrument	Requested days	Allocated days	From	To
D2B	2	2	07/09/2016	09/09/2016

Abstract:

Acidic zeolites are used in the chemical and petroleum industry because of their catalytic activity, reaction selectivity, and chemical and thermal stability. Neutron diffraction is best experimental method to probe Brønsted siting and it was used by our group to characterize acidic ferrierite, mordenite and heulandite(data collected at ILL, line D2B).The aim of this proposal is to determine the number and location of Brønsted sites in zeolite L, a large pore material whose acidity influences the photophysical behavior of encapsulated dyes and can affect the properties of photonic antenna systems based on dye–zeolite host–guest materials. We plan to collect two samples: the first exchanged with ND4 and then calcined at 550°C(D-LTL).Part of this will be then washed with D2O to obtain its acidic rehydrated form (RD-LTL).The data will be processed by the GSAS package. The protons location in D-LTL will provide essential information on the accessibility to molecules of Brønsted sites within the zeolite channels.The RD-LTL study will provide a complete understanding of both the hydrogen bonding network and the degree of confinement of zeolitic water in LTL

EXPERIMENTAL REPORT

EXPERIMENT N° 5-22-744

DATES OF EXPERIMENT: FROM 07/09/2016 TO 09/09/2016

TITLE: LOCATION AND MOBILITY OF ACIDIC PROTONS IN ZEOLITE L BY NEUTRON POWDER DIFFRACTION

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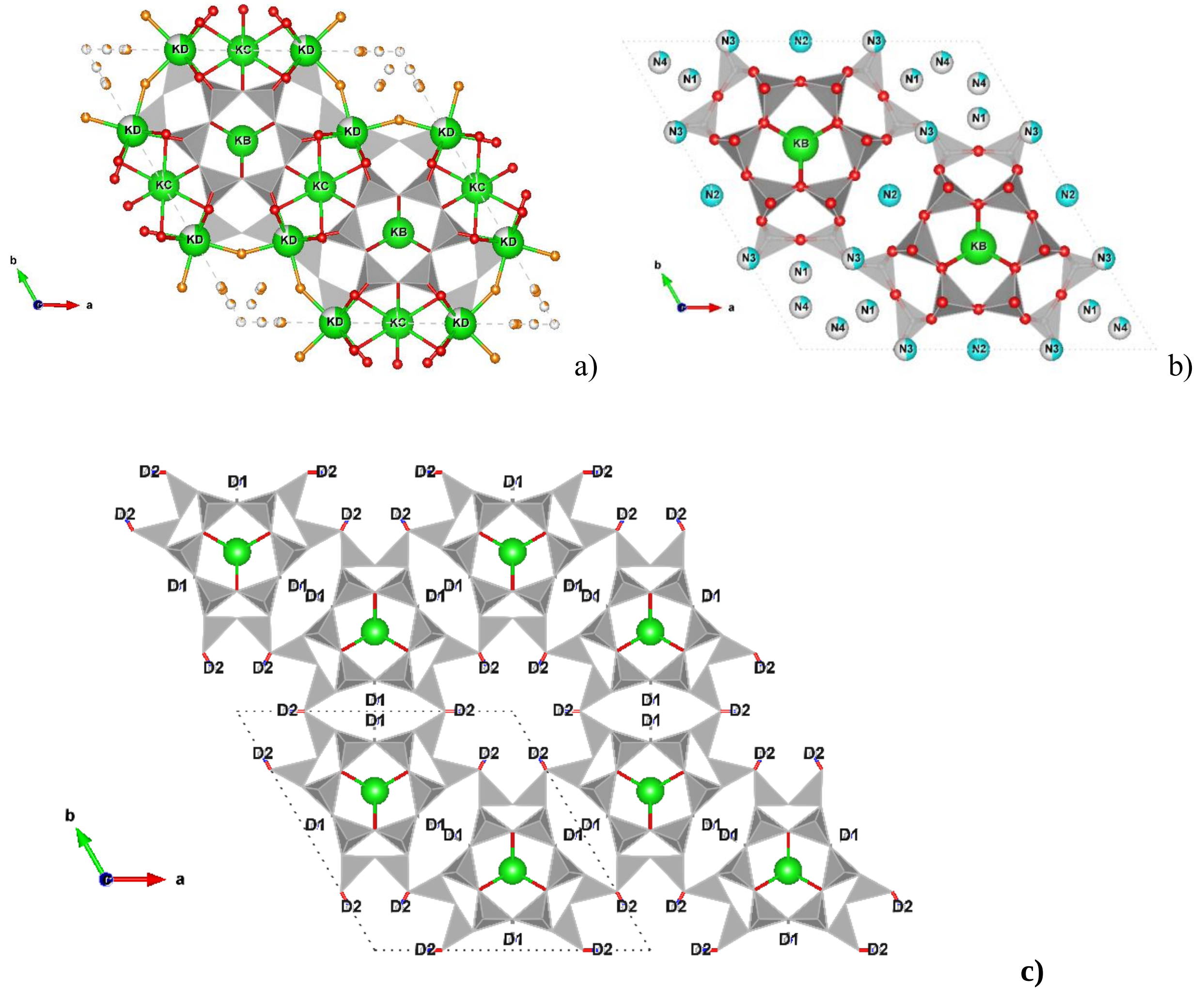
The aim of this proposal is to determine the number and location of Brønsted sites (BAS) in zeolite L, the synthetic counterpart of natural perlialite, via powder neutron diffraction. The information gathered by this experimental approach can provide a complete understanding of the role and behavior of BAS in the catalytic reactions involving this interesting zeolite.Zeolite L is a large pore material with ideal formula $K_6Na_3Al_9Si_{27}O_{72}21H_2O$, framework type LTL, s.g. P6/mmm, unit cell dimensions a = 18.40(4) Å and c= 7.52(3) Å). Its framework is built from columns of cancrinite cages stacked with double six membered rings (D6R) along the c axis. This peculiar arrangement creates large undulating 12-ring (12MR) channels, which are separated from each other by elliptical 8-membered ring channels, parallel to the original columns along the c-axis. The sample used in this project is a synthetic commercial zeolite L in its K form, obtained from Tosoh (code 500KOA namely L-LTL from now). The SiO_2/Al_2O_3 ratio (SAR) is equal to 6.1. The Na_2O and K_2O contents were 0.25 wt.% and 16.8 wt.%, respectively. The surface area (BET, m2/g) is 290 m^2/g. The L-LTL form was exchanged with 1 M ND_4NO_3 aqueous solution for ≈140 h at room temperature in order to obtain the acidic precursor (ND_4-LTL). Subsequently, the sample was filtered and heated under vacuum for 24 h at 600°C to remove ND_3, then washed with D_2O and dried overnight at 96 °C (D-LTL). LTL, ND_4-LTL and D-LTL samples were packed in an argon-flushed glove-bag into a vanadium container sealed with a rubber gasket and six screws to ensure humidity-free transport to the neutron source. Neutron data were collected at low temperature (2.25 K) on the high-resolution two-axis powder diffraction beamline D2B (wavelength = 2.398 Å, 4.0–150 2θ range) of the Institut Max Von Laue-Paul Langevin (ILL, Grenoble). Rietveld structure refinements were performed in the *P6/mmm* space group (Tab.1) by the GSAS-EXPGUI program [1-2]. For all structural refinements, the Bragg peak profile were modelled using a pseudo-Voigt function with a 0.01% cut-off of the peak intensity. The background curve was fitted using a Chebyschev polynomial with 20 variable coefficients. The refined parameters were the following: 2θ-zero shift, scale factor, unit-cell parameters, fractional coordinates, occupancy factors and isotropic displacement factors for both framework and extraframework atoms. Soft constraints were initially imposed on T-O (*i.e.*, 1.62 Å and 0.04 Å tolerance value), and D-O (*i.e.*, 1.00 Å and 0.04 Å tolerance value) distances and then relaxed in last cycles. The location of protons and extraframework species was carried out by a combination of least squares and Difference Fourier map techniques. The L-LTL crystal structure was determined by the Rietveld method in the P6/mmm space group. According to Newsam [3] the refined bond lengths suggested that the (Si, Al) distribution is not random (T1-O<1.640>Å; T2-O<1.654>Å), and indicated that Al is preferentially located in site T2 site. The enrichment of Al in T2 site was also revealed by the refined tetrahedral occupancies confirming that neutron diffraction is a good tool for the differentiation of Si and Al due to their different scattering lengths (b(Al)=3.449 x 10-15 m, b(Si)=4.149 x 10-15 m). Rietveld structural refinement allowed us to detect 18 water molecules per unit cell (corresponding to ≈11.3 % dry weight) spread over five partially occupied extraframework sites (Figure 1a). They are located in the main channel thus forming a succession of clusters with partial regularity and hydrogen bonded to O1 framework oxygen atom (O1-W3 3.228(15) and O1-W4 2.807(16), respectively). After ND4-exchange, no evidence of symmetry changes was found consequently the same P6/mmm space group as in L-LTL was adopted for this structure refinement. Framework atoms of LTL provided the initial parameters for determining the structure of ND4-LTL sample. Rietveld refinement indicated a small but significant increase in unit-cell parameters with respect to the as-synthesized zeolite (L-LTL: a = b= 18.3746(11) Å, c = 7.5270(6) Å, V= 2200.84(25) Å3; ND4-LTL: a =b= 18.4202(10) Å, c = 7.5402(5) Å, V= 2215.67(23) Å3) in agreement with other NH4-exchanged zeolites (Figure 1b). After ND_4-ion exchange the average T-O distance is nearly unchanged with respect the L-LTL sample (<T1-O>1.646 Å and <T2-O>1.650 Å in ND4-LTL, <T1-O>1.640 Å and <T2-O>1.654 Å in L_LTL, respectively) and the mean T-O-T angles are only slightly different (143.1° and 141.9° in ND4-LTL and L-LTL. Two Brønsted acid sites were recognized in D-LTL (Figure 1c) and their positions were firstly constrained geometrically (O-D=1.00 Å), restrains imposed were then relaxed in last cycles of refinement, and both deuterium atom coordinates and occupancies were allowed to refine independently. The first proton site, D1, is on framework oxygen O5 pointing towards the centre of 8MR channel; the second one, D2, is on the framework oxygen O1 pointing towards the 12MR. Enhanced increase in T1-O1 and T2 -O5 distances confirmed the effects of proton attractive force on framework oxygens. In figure are reported the location of extraframework sites in all investigated samples.



a) b)

c)

Figure 1. Location of extraframework sites in L-LTL (a), ND_4-L and D-L (c) zeolites, respectively.

References

[1] Larson, A. C.; Von Dreele, R. B. GSAS. General Structure Analysis System. LANSCE, MS-H805, Los Alamos, New Mexico, 1994; [2] Toby, B. H. EXPGUI, a Graphical User Interface for GSAS. J. Appl. Crystallogr. 2001, 34(2), 210-213; [3] Newsam, J. M. (1987). Aluminium partitioning in zeolite L. Journal of the Chemical Society, Chemical Communications, (2), 123-124.